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SPECIATION, TOXICITY AND TREATMENT OF ARSENIC IN A GOLD MILL EFFLUENT

by
Rob Marsland

A Thesis
Submitted to the Faculty of Graduate Studies and Research in Partial Fulfilment of the Requirements for the Degree of Master of Science
In
Environmental Engineering
Department of Civil Engineering

Edmonton, Alberta
Spring 1991

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ISBN 0-315-66606-4

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This letter is to confirm that you have my permission to make use of figures from my paper, 'Tailings Management Program - An Operating Success, Echo Bay's Lupin Mine,' presented at Seminars on Gold Mining Effluent Treatment, sponsored by Environment Canada in February, 1989 in Vancouver, B.C.. The figures referred to are the 'General Site Plan Lupin Mine,' the 'Tailings Impoundment Area - 1988' and the 'Schematic Cross-Section of Typical Syphon at 'J' Dam'. This copyright permission is intended solely for you to make use of these figures in your thesis. Thank you for showing such an interest in this work.

Yours sincerly,

Hugh R. Wilson, C.E.T.
Manager, Environmental & Regulatory Affairs

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DEGREE: Master of Science

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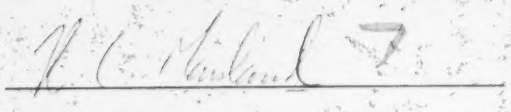

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Speciation, Toxicity and Treatment of Arsenic in a Gold Mill Effluent** submitted by **Rob Marsland** in partial fulfillment of the requirements for the degree of **Master of Science** in **Environmental Engineering**.

Dr. P.M. Huck

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Dr. J.A. Plambeck

Date: April 5, 1991

Abstract

The levels and speciation of the inorganic arsenic in the Lupin gold mill were studied. The ratio of As(V) to As(III) increased through the process and peaked in the tailings pond, prior to arsenic removal by ferric sulphate addition. Total arsenic levels are highest in the barren solution, and lowest in the treated tailings. An evaluation was made of the LC50 for rainbow trout on treated tailings water spiked with arsenic. The value obtained for As (III) agreed well with literature values. A review of the literature regarding the stability of arsenic bearing sediments was performed. It was concluded that the residual mineral arsenic (arsenopyrite) was likely to be thermodynamically unstable under oxidizing conditions while the arsenic bearing ferric hydroxide precipitate was likely to be unstable under reducing conditions. The former was confirmed qualitatively by a laboratory leach test.

Acknowledgements

Thanks to Dave Hohnstein, Wayne Zigarlick and Hugh Wilson of Echo Bay Mines. Thanks also to Dr. Peter M. Huck, Department of Civil Engineering, University of Alberta. Thanks to David Rector, Steve Stanley, Greg Milne and John Wild for the many lengthy discussions.

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1.0 INTRODUCTION

Arsenic and gold are found together in several parts of the world, and are commonly associated in sulphidic gold deposits in Canada and the western United States. The arsenic in these deposits is usually present as arsenopyrite (FeAsS). Gold present in arsenical ores is often difficult to recover (refractory).

Refractory ores require special processing to enhance recovery. Many gold recovery operations roast the ore by heating it to high temperatures in the presence of oxygen to oxidize the sulphur to facilitate the subsequent dissolution of the gold from the calcine (roasted ore). In this pyrometallurgical process, most of the arsenic exits with the stack gases, from which it is scrubbed.

Gold can be extracted by dissolving it in a cyanide solution. Direct cyanidation, where the cyanide is applied to the crushed and ground ore without any additional processing such as roasting or flotation, is feasible only when the gold is non-refractory. In hydrometallurgical processes most of the arsenic remains undissolved in the mineral (gangue) tails solids, which is the case at Echo Bay Mines' Lupin, N.W.T. operation.

Both hydrometallurgical and pyrometallurgical processes produce an arsenic bearing aqueous stream (i.e., tailings) which requires treatment. Arsenic is a polyvalent non-metal and has exceedingly complex chemistry. This complexity makes speciation of the arsenic very important for both treatment and toxicity. Arsenic can exert a toxic effect at very low levels.

The current treatment of the Lupin tailings involves separation of the solid phase, by settling, and treatment of the aqueous phase, with ferric sulphate. The treatment produces insoluble ferric hydroxide precipitate with adsorbed arsenic. This precipitate and the tails solids are the two arsenic bearing residues retained in the tailings impoundment basin.

1.1 Objective

The objective of this project was to improve understanding of the arsenic removal process and of precipitate stability in the Lupin tailings pond, with a view to providing information for a long term management approach to arsenic disposal. Practical investigations were made in four distinct areas.

1) Speciation of arsenic at Lupin. Arsenic can be present in water in trivalent (As(III)), pentavalent (As(V)) or organic forms. The literature suggests that arsenate (As(V)) is more readily removed from aqueous solution and is less toxic than arsenite (As(III)). It was believed that 85% of the total arsenic at Lupin is in the pentavalent form (Wilson, 1989b). Several sampling campaigns were conducted over the summer to determine how the concentration and speciation of arsenic vary throughout the process.

2) Aquatic toxicity of Lupin tailings. A series of bioassays was conducted on rainbow trout fingerlings to determine what arsenic concentration in the pond water would result in the death of 50% of the organisms (LC_{50}). Pond 2 water was used in the tests, with and without the addition of As(III) or As(V).

3) Critical examination of the current treatment scheme. The effects of mixing were studied to determine whether rapid mixing in the syphons is adequate for coagulation, and whether flocculation is required. Iron coagulant (Ferri-Floc) dosage was examined to see if higher doses would improve removal, and to evaluate the sensitivity of the operation to fluctuations in dosage.

4) Stability of the Sediment. Arsenic occurs in the tailings pond both as undissolved minerals from the ore (arsenopyrite and löllingite) and as ferric hydroxide precipitate from the treatment process. Since abandonment requirements insist that the total arsenic concentration in tailings pond runoff, in the future, does not exceed the current allowable discharge level, it is essential to determine the likelihood of future solubilization of arsenic. Of particular concern is the influence of pH and pε (oxidizing or reducing conditions) on stability. Oxidizing conditions exist in well aerated surface water. Reducing conditions can result from oxygen depletion of the water caused by microbial activity. The examination of microbial activity *per se* was outside the scope of this project, but a literature review examined the effects of oxidizing and reducing conditions on the stability of the aforementioned arsenic bearing residues. A four day laboratory leach test was performed to provide qualitative confirmation of the trends expected from the literature review.

2.0 BACKGROUND

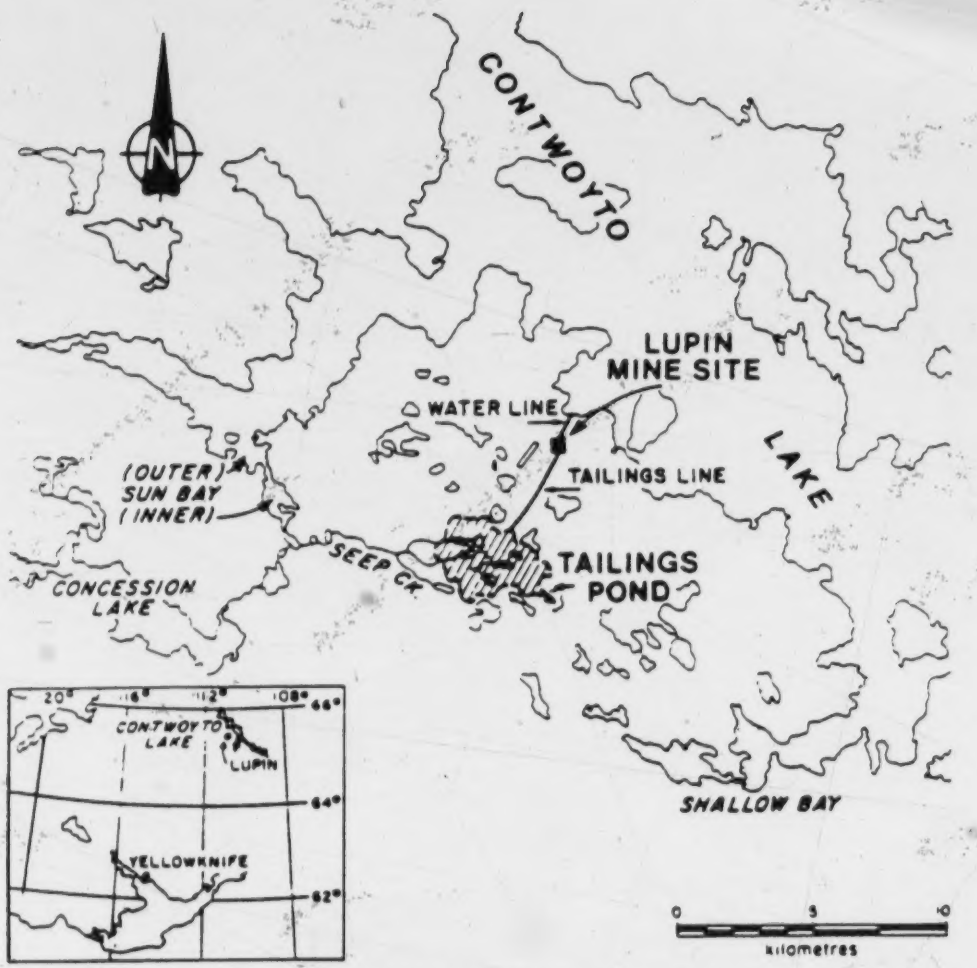
Echo Bay Mines' Lupin mine is located on the western shore of Contwoyto Lake approximately 80 kilometres south of the Arctic Circle in the barrenlands of the North West Territories, Canada. Figure 2.1 illustrates the geographical relationship between Lupin and Yellowknife (the capital of the NWT) and between the mill site, the lake and the tailings impoundment area.

The mill commenced commercial production in April of 1982, with a substantial expansion program started in 1983. Current throughput is about 1750 tonnes of ore per day. The gold extraction process consists of crushing and grinding (rod and ball mills) to 80% passing 200 mesh, followed by a three step alkaline pre-aeration stage. The cyanidation stage is carried out in 6 tanks in series with a mean residence time of 25 hours. After cyanidation the residual solids are separated from the gold laden pregnant solution and sent to the tails. The gold is removed from the pregnant solution through the Merril-Crowe process by the addition of zinc dust. The barren solution is separated from the gold precipitate in a pressure filter and bled to tails to control the levels of undesirable solutes. The arsenic concentration of the barren varies from 10 to 20 mg/L. The gold is smelted in a bullion furnace. A more thorough general description of the process is presented by Fulcher and Kim (1986).

The washed solids and the barren bleed are combined in the tails sump and pumped six kilometres to the 750 hectare tails impoundment area. Approximately 620,000 tonnes of solids and 1.1 million cubic metres of water

Figure 2.1

Source: Wilson (1989a)



GENERAL SITE PLAN
LUPIN MINE

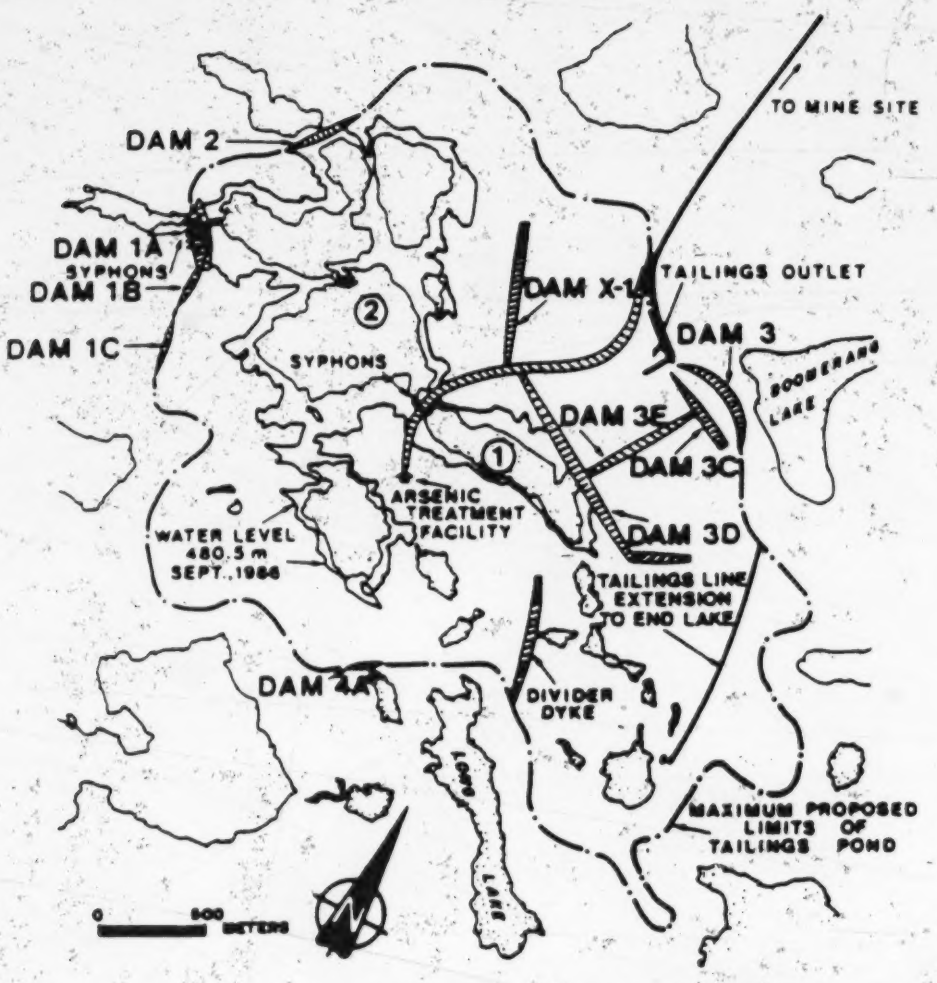
are pumped to the tailings pond, annually, based on the Lupin mill's monthly pumping reports.

The tailings pond has been designed to incorporate a three stage treatment process. Firstly, the tails solids are allowed to settle out in the solids retention pond (SRP) and the tails solution is accumulated over the year in Pond 1. Once a year, in late August, Pond 1 is drained down into Pond 2, at which time the ferric sulphate is added for arsenic removal. The treated water is detained in Pond 2 until the following July when it is discharged to the environment. Figure 2.2 shows the approximate layout of the tailings ponds in the summer of 1989.

Table 2.1 shows the average decant (from Pond 1), the average discharge (from Pond 2) and the discharge limit concentrations. Pond 1 values exceed the discharge limits for arsenic, cyanide, copper and zinc. However, after treatment and the subsequent year long detention in Pond 2, the final discharge from Pond 2 easily meets all of the water quality requirements.

Figure 2.2

Source: Wilson (1989a)



TAILINGS IMPOUNDMENT AREA - 1988

Table 2.1

Water Quality Parameters Regulated by NWT Water Board

All in mg/L except pH	Discharge Limits * Ave	Max	1986 Pond 1	1987 Pond 2	1987 Pond 1	1988 Pond 2	1988 Pond 1	1989 Pond 2
Total Arsenic	0.50	1.00	2.11	0.23	1.43	0.34	1.65	0.41
Total Cyanide	1.00	2.00	9.48	0.30	17.2	0.06	3.29	0.067
Copper	0.30	0.60	1.84	0.28	2.75	0.068	1.646	0.024
Lead	0.05	0.10	<0.01	<.004	<.005	<.005	<.005	<.005
Nickel	0.10	0.20	0.14	0.056	0.198	0.047	0.182	0.055
Zinc	0.50	1.00	2.21	0.098	3.29	0.113	0.38	0.12
Suspended Solids	15.0	30.0	7.0	13.0	9.12	8.3	8.0	5.3
pH	>6.0	>6.0	8.93	7.43	9.12	7.35	8.12	7.28

All are in units of mg/L except pH

All data from one or more samples analyzed at the Lupin Environmental Laboratory.

*Source: Echo Bay Mines Water Licence N7L3-0925 - Licence expires May 31, 1990, a new permit has been issued.

Note: In 1987, Pond 1 was treated in July, while Pond 2 was discharged simultaneously.

3.0 LITERATURE REVIEW

3.1 Arsenic Speciation

Arsenic is present at some level in all surface waters. It is a widely distributed element and is currently believed to be essential to life at very low concentrations (Emsley, 1985).

Arsenic (V) is the predominant form of arsenic in oxygenated waters. Thermodynamic equilibrium in seawater at pH 8.1 has been calculated to have an As(V)/As(III) concentration ratio of 20^{26} (Johnson, 1981 in Eisler, 1988). However, arsenic in ocean water has been measured to be speciated 80% as As(V) (Ferguson and Gavis, 1972), while oxygenated lake water has been reported to contain 10% arsenic (III) (Seyler and Martin, 1989). The measured difference is caused, in part, by the slow kinetics of arsenic oxidation but it is, more importantly, because of competing reverse reactions which are biologically mediated (Comber and Howard, 1989). Consequently, even in water in which arsenic (III) is not thermodynamically favoured, As(III) can represent a measurable percentage of the arsenic present.

Arsenic is also incorporated into organic molecules, such as monomethylarsonic acid and dimethylarsinic acid (cacodylic acid), usually by bacteriological action (Seyler and Martin, 1989). The frequent occurrence of organic arsenic compounds in natural waters demands that these compounds be tested for specifically, in any water quality analysis, as they are not quantatively recovered by the usual methods for arsenic determination (Hinners, 1982). As this project dealt exclusively with process water drawn from deep in an arctic lake, which should have little biological activity

because of the lack of nutrients, it was believed to be unnecessary to perform special analyses for organo-arsenical compounds.

3.2 Analytical Methods

3.2.1 Total Arsenic Determination

Total arsenic determination procedures have long made use of hydride generation. The nascent hydrogen required for arsine production was formerly produced by the reaction of metallic zinc with acid (HCl). However, this reaction is rather slow (30 minutes) and was not conducive to examination of large numbers of samples (Robbins and Caruso, 1979; APHA-AWWA-WPCF, 1989). In the early 1970's, use of sodium borohydride ($NaBH_4$) reacted with acid, as the reductant, came to the forefront. The reaction can be described as follows:

$$NaBH_4 + 3H_2O + H^+ \rightarrow H_3BO_3 + Na^+ + 8H\cdot \xrightarrow{As^{3+}} AsH_3 + H_2 \text{ (excess)}.$$

This reaction is quite rapid (10 to 30 seconds) from an aqueous solution of $NaBH_4$ ranging from 0.5% to 8% w/v in concentration. Use of an aqueous solution potentiates development of a continuous hydride generation process (Robbins and Caruso, 1979).

Prior to widespread acceptance and use of atomic absorption techniques, the arsine was absorbed into a solution of silver diethyldithiocarbamate dissolved in pyridine. This formed a soluble, red, complex suitable for spectrophotometric analysis (APHA-AWWA-WPCF, 1989). With the advent of the highly element specific atomic absorption spectrophotometry (AAS) it appeared that hydride generation would become

unnecessary. However, because of the short wavelength (far UV) of the optimal analytical absorption line for arsenic, high levels of background absorption were encountered when utilizing direct solution nebulization into an entrained air-acetylene flame (Robbins and Caruso, 1979). Thus, much lower levels of arsenic can be measured through hydride generation.

Since most arsenic analysis is done at very low levels, it is necessary to ensure low levels of background noise to lower the detection limit. There are various ways in which the basic AAS with hydride generation process has been modified over the years to try and optimize the signal strength.

Using hydrogen as fuel and using nitrogen or argon for a carrier gas, both provide a much more stable flame, and hence signal, than the traditional entrained air-acetylene flame. An electrically heated graphite furnace can also be used. Another frequent modification is to introduce the arsine gas into a quartz atomisation tube mounted in the optical path of the AAS. This cell is then heated externally by flame or electrical wire or internally by a fuel rich oxygen-hydrogen flame.

The lowest detection limits have been achieved by using the above modifications in combination with a liquid nitrogen trap. After the arsine is generated, the vapour stream is passed through a U-tube cooled with liquid nitrogen. Once all of the arsine has condensed out, the trap is rapidly warmed and the arsine is entrained or aspirated into the AAS. Detection limits of a few tenths of a nanogram per litre have been obtained (Comber and Howard, 1989; Andrae, 1977).

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) can also be used but this gives a much higher detection limit (~50μg/L) than

hydride generation with AAS, although the ICP can also be used with hydride generation (Pruszkowska, 1983).

In more recent years most of the developmental work has related to devising a method for continuous arsine generation. The basic principles for hydride production are the same whether the generator is hooked to an ICP (Pruszkowska, 1983), Direct Coupled Plasma (DCP)-AES (Ek and Huldén, 1987) or an AAS with an electrically (Comber and Howard, 1989; Arbab-Zavar and Howard, 1980; Agemian and Bedek, 1980) or flame (Brodie et al., 1983) heated quartz atomisation cell.

Comber and Howard (1989) and Arbab-Zavar and Howard (1980) used a liquid nitrogen trap to facilitate organic arsenic determination. This is possible because of the different boiling points of the arsines. However it does not allow differentiation between arsenic (V) and arsenic (III).

To ensure quantitative recovery of As(V) from the sample, it is imperative to make use of a pre-reduction step. The sample is diluted with a 1% solution of sodium or potassium iodide in 10% HCl (APHA-AWWA-WPCF, 1989) which reduces the As(V) to As(III). The arsenic (III) is then reduced to arsine gas in the hydride generator by the $NaBH_4$. Some attempts have been made to combined the pre-reduction step with the hydride generation step in the continuous process (Crock and Lichte, 1982) but it is believed that the pre-reduction step is too slow to be used in a continuous flow process (APHA-AWWA-WPCF, 1985).

The continuous method for arsenic determination has a number of advantages over the traditional batch method. The primary advantage is the increase in sample analysis rate, 30 samples per hour can easily be measured

(Comber and Howard, 1989). Secondary advantages include the incorporation of any blank response from HCl contamination into the background baseline and removal of the effect on light-path transparency of the sudden influx of hydrogen which occurs in the batch process (APHA-AWWA-WPCF, 1989). APHA-AWWA-WPCF (1989) now has a proposed continuous method, which is especially recommended for selenium determination, that can also be used for total arsenic analyses.

3.2.2 Arsenic (III) Determination

Hydride generation is also used for arsenic (III) determination, however two important modifications are made. Obviously it is no longer necessary to pre-reduce the As (V), but a more subtle complication is the partial recovery of As(V) at low reaction pH. Aggett and Aspell (1976) were the first widely received authors to distinguish between As(III) and As(V) using AAS with batch hydride generation. Their work illustrated that pH control was essential for good As(III) recovery while preventing As(V) recovery. They showed acetate buffer was more appropriate than citrate buffer, as there were fewer interferences. As the inorganic arsine (AsH_3) generated is identical, use of a liquid nitrogen trap does not discriminate between inorganic arsenic species.

3.2.2.1 As(V)/As(III) Discrimination

Determination of arsenic (III) in the presence of arsenic (V) at an As(V)/As(III) ratio of 40:1 at pH 3.5 and 50:1 at pH 5 was possible. Below pH 3.5, As(V) recovery becomes excessive, and above pH 5, As(III) recovery becomes less than quantitative (Aggett and Aspell, 1976). However, Hinners (1980) warns that there is not only the potential for recovery of organic arsenic

but also for the recovery of As(V), at any pH. That study found recovery of As(V) to contribute 60% of the signal strength at an As(V)/As(III) ratio of 33:1 (600 µg As(V)/L and 18 µg As(III)/L). Andrae (1977) also reported recovery of As(V) at the pHs used to determine As(III). As it was believed that As(V)/As(III) ratios at Lupin would be much lower than 33:1 (i.e. 85% As(V) to 15% As(III) or 6:1 (Wilson, 1989b)), this undesirable recovery of As(V) was not anticipated to be a problem.

3.2.2.2 pH Control

Hinners (1980) used a batch generation method with a 2 M, pH 4.8 acetate buffer for all studies. This resulted in a 1 M acetate concentration after dilution by the sample and borohydride solution. Aggett and Aspell (1977) used a 0.5 M buffer to control the pH to within 0.25 of pH 4, also in a batch reactor. Comber and Howard (1989) used a continuous generation method with a 0.1 M, pH 5.0 buffer with a liquid nitrogen trap which was, hence, actually a semi-continuous system. Seyler and Martin (1989) used a batch method with a 1 M, pH 4.8 acetate buffer. No studies of arsenic (III) determination by continuous hydride generation, without the use of a cold-trap, were found, presumably because of the problems with arsenic (V) recovery. Comber and Howard (1989) make no mention of encountering any difficulties in differentiating between As(III) and As(V) at As(V)/As(III) ratios as high as 50:1. Seyler and Martin (1989) were working at As(V)/As(III) levels around 10:1.

(probits). When these probit responses are plotted against the log of the doses (concentrations), a straight line results (if all the assumptions hold true). The log of the concentration is used because it is presumed, from empirical data, to give the straightest line. Use of the probability scale prevents the unwarranted calculation of an LC_0 or LC_{100} as these absolutes cannot be determined from this treatment of the data.

The LC_{50} as well as the LC_{10} and LC_{90} can now be calculated from the regression coefficients. However it must be remembered that the confidence interval will widen dramatically towards the ends of the line. The slope of the dose-response curve is also obtained. A 'flat' dose-response curve indicates that a large change in concentration is required before a significant change in mortality will occur, whereas a 'steep' response curve indicates that the death rate is relatively sensitive to changes in toxicant concentration (i.e. for a steep dose-response curve a small decrease in concentration will dramatically reduce the death rate but a similar decrease in concentration for a toxicant with a flat dose-response curve will have little effect on mortality).

From the data accumulated during a 96 hour (96-h) acute toxicity test, it is possible to make first estimates of median threshold acute toxicity. That is the minimum concentration which will cause the death of 50% of the test population regardless of the test duration. It is also possible to extrapolate the dose-response curve down to low dose levels to facilitate a first estimate of the death rate at low concentration. Again it must be stressed that the confidence limits in this range are very large (probably at least an order of magnitude) and that the values obtained are applicable only to the species tested.

The LC/LD_{50} is not intended to show that a chemical is safe, but rather to characterize the extent of the hazard. However, EPA and other standards are often set as 10% of the 96-h LC_{50}. To estimate a 'safe' concentration of a toxicant, it is necessary to perform chronic (long-term) toxicity tests. From these studies it should be possible to determine the maximum concentration at which no toxic effect is observed (NOEL - No Observable Effect Level) and the lowest level at which a response is observed (LOEL - Lowest Observable Effect Level). Obviously the criterion of response for these tests is not death but rather some degree of adverse effect (i.e., some adverse effect or no adverse effect). The toxic effect curve need not parallel the lethal effect curve which means that the changes in response may not correspond at the differing dosages.

Unfortunately, the data generated from a standard acute toxicity test cannot be directly applied to any other population. Because of the genetic diversity of life, the LC_{50} is dependent on the species, strain, sex, age, weight, condition, degree of acclimation and diet of the test organisms. It is also dependent on environmental conditions such as chemical properties of the test solution (including the dilution water), temperature and other physical properties of the test solution, the number of test species in the test container, the toxicant loading rate (mg of toxicant per mg of test population) and the test duration (Casarett and Doull, 1986; APHA-AWWA-WPCF, 1989; White and Champ, 1983). The bioassay is the usual experimental method for determining toxicity. To best use the data collected in such a test it is essential to "define the problem carefully and succinctly and establish how the results of the toxicity test will assist in the problem solution" (APHA-AWWA-WPCF, 1989).

Bioassays can be of both short term (acute) duration (≤2 weeks) and long term (chronic) duration (90 days to 3 years). The 96-h acute toxicity test to determine the median lethal concentration (LC_{50}) is the most common. The 96-h test duration is selected as this is usually sufficient time to allow the test organisms to achieve biological equilibrium with their local environment (and it fits conveniently into a North American workweek). This then allows an estimation of the threshold LC_{50} which can eliminate test duration as a variable. The median lethal concentration is chosen because it is the mid-point on the regression line and has the tightest confidence interval.

3.3.2 Fish Bioassays

Fish are commonly used when determining LC_{50}'s as they are macroscopic and it is relatively easy to distinguish between living and dead organisms. Rainbow trout (*Salmo gairdineri*) are ubiquitous in the large lakes around Lupin and are widely used as standard reference organisms, and so were an obvious choice of test species. This species name has recently been changed to *Oncorhynchus mykiss*, however the literature referred to in this work used the old name and that tradition will be continued herein, for consistency.

An important choice in an acute toxicity test is whether to run it as a static test or as a flow through test. The flow through test provides a continuous flow of fresh toxicant. This is particularly important for toxicants which are removed appreciably from solution by chemical precipitation or biological absorption. Arsenic bioconcentrates in most fish by a factor of less than 17 (EPA 1980, 1985 reported in Eisler, 1988). This is relatively low and would have negligible effect on the arsenic concentration in the test container if the mass loading rate (i.e., total mass of test organisms per container volume) is

reasonably low (<0.8 g/L). Physicochemical removal of arsenic from solution could occur if there are high concentrations of humic substances or iron hydroxide precipitates. Use of dechlorinated drinking water as dilution water minimizes these as possible effects at higher levels of dilution and helps to ensure that the test organisms are responding to the dose of arsenic rather than some extraneous contaminant.

Unfortunately, the use of drinking water introduces other variables since it may have little in common with the local water, depending on circumstances. Most importantly, it prevents any knowledge of the synergistic or antagonistic effects that may be had from the other constituents of the tailings discharge. Copper and cyanide are both particularly lethal to many species of fish. This suggests the use of on-site and *in situ* tests. These have the advantages of more closely representing the local environmental conditions.

The *in situ* test is performed by caging the test organisms and placing them directly into the discharge at various points downstream, to vary the degree of dilution. However, that degree of dilution is difficult to quantify. The on-site tests are laboratory tests where the dilution water is taken from 'upstream' of the discharge. This method is better controlled and reduces the risk of infection and the effects of other externalities.

3.4 Health Effects of Arsenic

Arsenic has long been known for its toxic potential, and it has both insidious chronic effects and a low acute lethal dose. Because of its highly complex chemistry, it can be absorbed into a biological system by inhalation, ingestion or through the skin.

3.4.1 Human

The polyvalence of arsenic allows it many different forms, which are absorbed by different routes. For example, arsine gas (AsH_3) is inhaled, while arsenate and arsenite can be either absorbed through the skin or ingested. The many forms arsenic can take also causes it to act through widely differing mechanisms. Arsenite reacts with sulphydryl groups of proteins resulting in enzyme inhibition (Demayo, et al., 1979). Arsenate may uncouple oxidative phosphorylation (Eisler, 1988) because of the similarities in chemical properties with phosphate (Vahter and Envell, 1983). Arsine acts quite differently as it is a haemolytic poison (Blackwell and Robbins, 1979). Excretion in the urine is the usual route for arsenic elimination. Methyl arsenics formed through biomethylation are the major urinary metabolites of inorganic arsenic. The most common are monomethylarsonic acid (20%) and dimethylarsonic (cacodylic) acid (60%) (Vahter, 1983).

Some reports quoted in Eisler (1988) give an arsenite (arsenic trioxide) LD_{50} of 1 to 2.6 mg As/kg body weight. Chronic arsenic poisoning has been found at 0.6 mg/L of total arsenic in drinking water. In a terrible tragedy in Japan, 12,000 infants were poisoned (128 deaths) by consuming an average of 3.5 mg As daily for one month in dry milk. Symptoms included "severe hearing loss, brainwave abnormalities and other central nervous system disturbances," 15 years after exposure (Pershagen and Vahter, 1979 in Eisler, 1988). An epidemiological study in Taiwan demostrated a possible relationship between the vascular "Blackfoot Disease" and other associated illnesses and the consumption of well water containing high levels of arsenic (Chen, 1988 in Hrudey and Hrudey, 1989).

Epidemiological studies have shown arsenic to be a human carcinogen. It has been positively linked to respiratory, skin and liver cancer, dependent on arsenic form and route of absorption. In 1980 the EPA calculated an increased level of risk of cancer in humans over a lifetime of 1 in 1,000,000 from eating fish which live in water contaminated with arsenic at a level of 0.0175 µg As/L (reported in Eisler, 1988). The same level of risk was obtained for drinking water containing 0.0022 µg As/L (reported in Eisler, 1988). All studies were based on chronic exposure, as acute doses tend towards rapid death or elimination of the toxicant and subsequent recovery (Dickerson, 1977? [Incomplete Reference]). Demayo, et al., (1979) report that these cancers take 25 to 40 years to develop. Unfortunately, no studies on animals have been able to simulate this carcinogenesis.

3.4.2 Rainbow Trout

Aquatic organisms are particularly vulnerable to the effects of arsenic present in industrial discharge. 96-h LC_{50} values for rainbow trout (*Salmo gairdneri*) have been reported by Spehar et al. (1980) to be in the range 23-26.6 mg/L for arsenic (III) (as reported in Eisler, 1988). Gilderhus (1966) reported an LC_{50} of 14.8 mg/L. Hale (1977) found the lowest acutely toxic concentration of arsenic (III) to be 10.8 mg/L (in Demayo, et al., 1979).

The acute toxicity of arsenic (III) has been found to be highly dependent on the age of the test organisms (Fowler, 1983) which would help to explain the differences between literature values.

A 28 day LC_0 for arsenic (V) was determined to be 0.97 mg/L by Spehar et al. (1980); there was no accumulation of arsenic at this level. This is very

similar to results from Johnson and Finley (1980) and NAS (1977) (reported in Eisler, 1988).

The LC_{50} values are known to be "markedly affected by water temperature, pH, Eh, organic content, phosphate concentration, suspended solids, and presence of other substances and toxicants, as well as arsenic speciation, and duration of exposure." In general, trivalent arsenic species are more toxic to aquatic biota than pentavalent species and early life stages are most sensitive (Eisler, 1988).

3.4.3 Current Regulations and Guidelines

The current Canadian drinking water guideline is 0.05 mg/L. The drinking water objective is 0.01 mg/L (CCREM, 1987). Lupin is presently allowed to discharge at an arsenic concentration of up to 0.5 mg/L or ten times the drinking water limit.

In 1985 the US EPA suggested a discharge limit to freshwater of 190 µg/L of arsenic (III). This is the 4 day mean concentration which is permissible no more than once every 3 years. The one hour mean is not allowed to exceed 360 µg/L. This level is regarded as too lenient for the prevention of adverse affects to freshwater biota (Eisler, 1988). The EPA has not suggested a specific guideline for arsenic (V), which is the major arsenic species in the Lupin discharge.

3.5 Current Treatment Practices

3.5.1 Evolution of Arsenic Removal Techniques

Arsenic was often removed from solution by the same processes used for heavy metals. Liming (addition of $Ca(OH)_2$) was the most popular of these (Smecht, et al., 1975). There are two problems with this technique. First of all, arsenic forms negatively charged species in water, at natural pHs, which is not removed from solution by addition of hydroxide. Secondly, the calcium arsenate which does form is not thermodynamically stable in the presence of carbon dioxide (Robins, 1982; Nishimura et al., 1988). The calcium arsenate reacts with the carbonic acid, caused by atmospheric CO_2 dissolving into the water, resulting in the formation of calcium carbonate and the release of arsenic into solution. This led to the wide spread use of iron compounds to remove arsenic (Lee and Rosehart, 1972; Rosehart et al., 1972; Robins, 1985).

Activated alumina has also been used for arsenic removal, usually from drinking water (Shen, 1972). It is often used as a point-of-use treatment method, which is a very small scale (Fox, 1989). Section 8.2 provides a brief list of references of activated alumina and other arsenic removal techniques.

3.5.2 Arsenic Removal by Iron Co-precipitation

This field has now been studied extensively in the literature. It is an important aspect of arsenic removal chemistry in both natural systems and industrial wastewater treatment. There is still some debate as to the exact removal mechanism. One view is that Fe-As precipitates which result in low arsenic concentrations in solution at normal pH involve the adsorption of

arsenic on ferric hydroxide and hydrated ferric oxide. These precipitates are amorphous in character and are very loosely bound thus offering vast areas for adsorption of the arsenic (Robins 1985, 1988; Robins et al., 1988). The adsorption is believed to occurr while the hydroxide is still in microflocs less than 0.5 nm in diameter (Robins et al., 1988; Cities Service, 1978; Merrill et al., 1986). This has caused this adsorption reaction to be referred to as a co-precipitation reaction (Merrill et al., 1986). However X-ray diffraction analyses have not shown the arsenic to be substituted for the iron (Robins et al., 1988), whereas with barium-radium sulphate co-precipitates, the radium chemically substitutes for the barium (Huck and John, 1989).

Krause and Ettel (1985, 1987) and Harris and Monette (1988) tend to disagree with the strictly absorptive mechanism. These researchers believe that a basic ferric arsenate is formed. Ferric arsenate is thermodynamically stable at pH 2, however the extra hydroxl groups are supposed to give stability over a wide range of pH. In their view, the arsenic is actually chemically bound into the complex, perhaps one step beyond the co-precipitation suggested by Merrill et al. (1986).

Regardless of the actual physical/chemical mechanism through which arsenic is removed by iron, it is unanimously regarded as an effective method for control of arsenic on an industrial scale.

3.5.3 Simulation of Coagulation and Flocculation by Jar Testing

The purpose of jar tests is to imitate actual operating conditions on a laboratory scale. Mixing in a vessel is traditionally measured by the time of mixing (t) and the velocity gradient or average mixing intensity (G). The

subjects of coagulation and flocculation are widely discussed in a number of common environmental engineering texts (Weber, 1972; Montgomery, 1985).

Cornwell and Bishop (1983) have developed nomographs relating impeller speed to the velocity gradient for two jar shapes and three impeller types. One of their figures corresponds exactly to the configuration used in this study, allowing easy scale-down/scale-up calculations. However, it must be recalled that these are still only very rough approximations to full scale practice, particularly considering the complete lack of geometrical similarity between the square gator jars with flat paddle agitators, and the tubular, continuous flow syphons, which entirely lack mechanical mixers.

3.6 Sediment Stability

3.6.1 Introduction

Ore at Lupin contains 1-1.2% arsenic by weight. This is mostly as the minerals arsenopyrite (FeAsS) and löllingite ($FeAs_2$) (Baum, 1988 and Lakefield, 1988). Of the 10 kg of As present per tonne of ore, approximately 1.5 g per tonne of ore actually goes into solution during the gold extraction process. The dissolved arsenic is then removed at the arsenic treatment stage by precipitation with ferric hydroxide. This material has been calculated to contain 3-4% arsenic by weight, based on an approximate Fe/As ratio of 18:1 and assuming all of the iron is present as $Fe(OH)_3$, with no significant amounts of other substituents such as sulphate.

Consequently, arsenic resides in the tailings area in two forms. There is a large quantity of arsenic in the undissolved mineral component of the tails solids, and a comparatively small quantity (1 tonne/year) of arsenic

adsorbed to the ferric hydroxide precipitate. Table 3.1 shows the relative quantities. These two types of arsenic bearing residue will behave quite differently in the post-operative scenario.

3.6.2 Thermodynamics of stability

The thermodynamic stability of combinations of selected elements can be evaluated quickly from the examination of a pε-pH (Pourbaix) diagram. These diagrams are prepared from Gibb's Free Energy data at a given temperature and given concentrations of consituents. They illustrate which compounds are stable under what redox conditions and pH. They are widely used in metallurgical processing especially in the steel industry, and are extremely useful.

As all of the reaction spaces of interest for this work necessarily contain water, two useful lines appear on all of the pε-pH diagrams. These are the lines which indicate the limits of thermodynamic stability of water.

The lower line indicates the combinations of E_h and pH in which the hydrogen ions from the dissolution of water will reduce to molecular hydrogen (H_2). The line is drawn through the equilibrium conditions where the rate of forward reaction (reducing to hydrogen) is equal to the oxidation back to hydrogen ions. The upper line corresponds to the equilibrium state of the oxidation of water. The oxygen/water line is about 20 pε units (1220 mV) above the hydrogen/water line.

3.6.2.1 Mineral Stability

Examination of a pε-pH diagram such as Figure 3.1 (Robins, 1985) shows that arsenopyrite is stable in water at neutral pH under low pε values.

Table 3.1

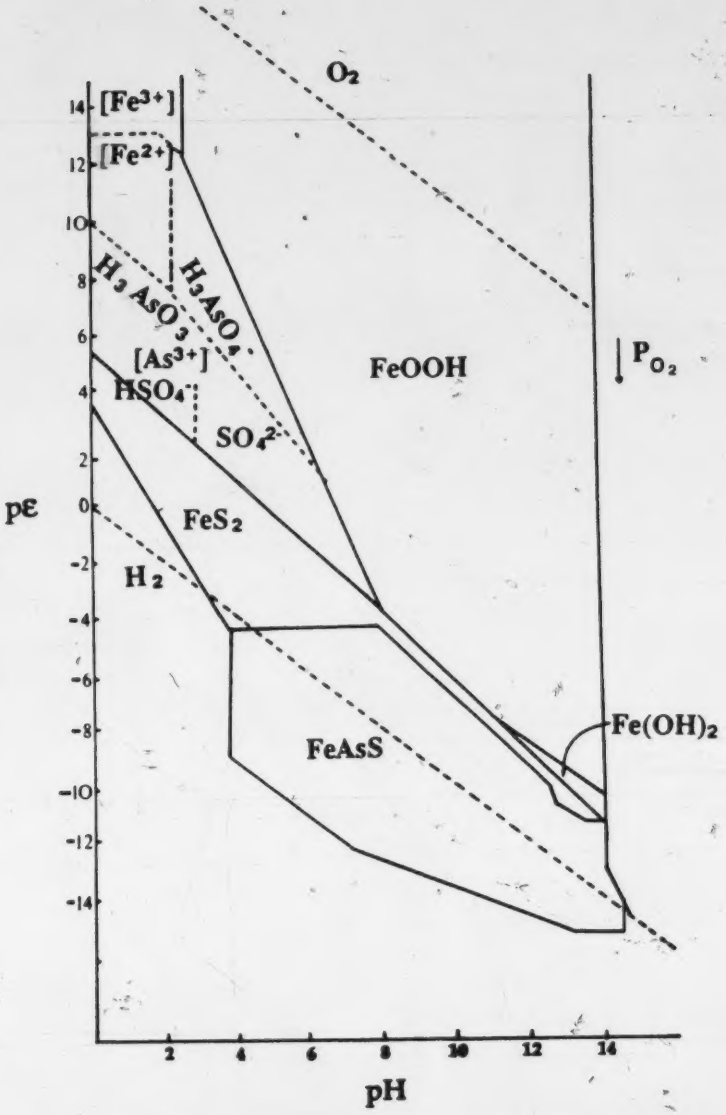
Annual Arsenic Deposition in Tailings Ponds

Mineral solids discharged to tailings pond	626 858 tonnes	(a)
Arsenic concentration in solids	1%	(b)
Arsenic contained in tails solids	6 269 tonnes	(c)
Volume of Pond 1 water treated	428 045 m^3	(a)
Difference in arsenic concentration from Pond 1 to Pond 2	2.2 mg/L	(c)
Arsenic contained in precipitate	0.941 tonnes	(d)

Sources:
(a) Lupin Annual Pumping Report
(b) External Laboratory Analysis (Baum, 1988 and Lakefield, 1988)
(c) Lupin Environmental Laboratory Analyses
(d) Calculated

Figure 3.1

After Robins, 1985, page 1.18, Figure 13



pε - pH Diagram for the Fe-As-S-Water System
where {Fe} = {As} = {S} = 10^{-4}
and $P_{H_2} = 1, P_{O_2} = 1$

$[S^{2-}] \approx 10^{-4}$M = 3.2 mg/L or 9.6 mg/L as SO_4^{2-}
whereas at Lupin SO_4^{2-} = 300mg/L or $[S^{2-}] \approx 10^{-3}$M

The pyrite oxidation line roughly parallels the hydrogen line, about 5 pε units (300 mV) above it. This represents the highest level of oxidizing conditions below which sulphur/iron species are stable (at a sulphur concentration of 10^{-4}M). At Lupin, the solids retention pond (SRP) decant water has been measured to have pH 9.5 and E_h=+250 mV (pε 10), whereas Pond 2 had pH 8 and E_h=+800 mV (pε 15). As part of this study, these data were gathered on August 25, 1989, and they probably vary throughout the year.

The absence of löllingite ($FeAs_2$) from this diagram shows that it is more soluble than other iron/arsenic compounds in the presence of sulphur. That is, the concentration of iron or arsenic needs to be greater than 10^{-4}M (5.6 mg/L Fe or 7.5 mg/L As) when total sulphur concentration is 3.2 mg/L, to form löllingite.

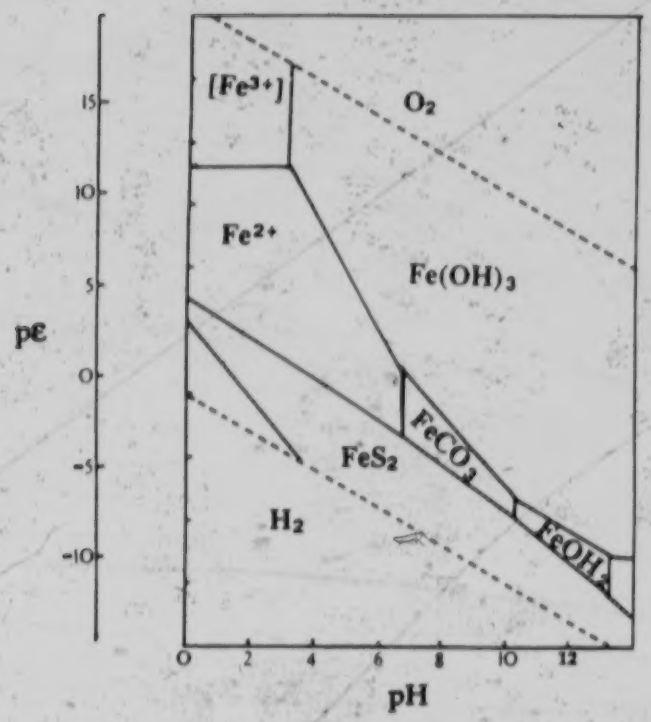
3.6.2.2 Precipitate

The ferric hydroxide precipitate, bearing adsorbed arsenic, is thermodynamically favoured (stable) at high pH in oxidizing conditions as shown in Figure 3.2. Its stability is a strong function of pH at pH<8 and strong function of pε at pε<-3 (pH>8). $Fe(OH)_3$ is not stable below pH 4 when the total iron concentration is $\leq 10^{-4}$M (5.6 mg Fe/L). Increasing the concentration to 5×10^{-4}M (~30 mg/L used at Lupin) lowers this pH limit by less than 0.25 pH units.

In addition, studies have shown that the arsenic does not remain tightly bonded to the amorphous precipitate when the pH goes above 8, although desorption is inhibited by higher iron doses (Krause and Ettel, 1985; Harris and Monette, 1988; Brannon and Patrick, 1987).

Figure 3.2

After Snoeyink and Jenkins, 1980; Figure 7-18



pε-pH Diagram Fe-S-C-Water System
25°C, 1 atm, $C_{T,S} = 10^{-4}$, $C_{T,CO_3^{2-}} = 10^{-3}$, $C_{T,Fe} = 10^{-4}$

$[S^{2-}] = 10^{-4}M = 3.2$ mg/L or 9.6 mg/L as SO_4^{2-}
whereas at Lupin $SO_4^{2-} = 300$mg/L or $[S^{2-}] = 10^{-3}M$

3.6.3 Kinetics of Chemical Leaching

Although both mineral and precipitate compounds have regions of thermodynamic instability (i.e., can release arsenic) which probably exist in the Lupin tailings pond, the kinetics of chemical oxidation (mineral) or reduction (precipitate) are quite slow.

3.6.3.1 Mineral

Stumm and Morgan (1981) illustrate the oxidation of pyrite as shown in Figure 3.3. They state that the oxidation of other pyritic minerals is similar. The key steps in the reaction shown are as follows:

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15\,Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \text{(fast)}$$

$$4Fe^{2+} + O_2 = Fe^{3+} \qquad \text{(slow)}$$

These correspond to the reactions

$$FeAsS + 11Fe^{3+} + 7H_2O = 12Fe^{2+} + H_2AsO_3^- + SO_4^{2-} + 12H^+$$

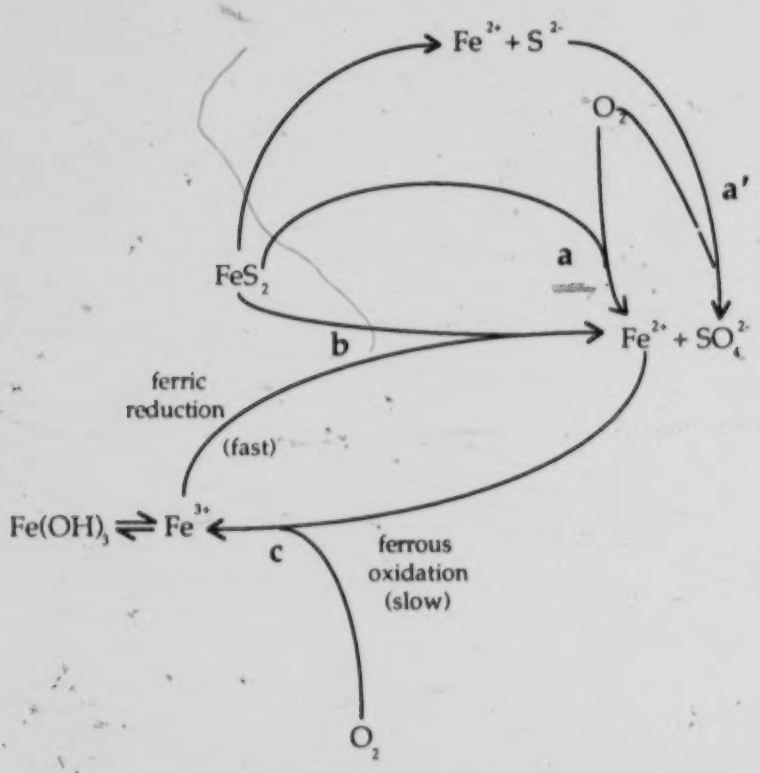
$$4Fe^{2+} + O_2 = Fe^{3+}$$

for arsenopyrite. The rate controlling step for both reaction pairs is the oxidation of ferrous ion to ferric ion.

The reduction of Fe^{3+} by (arseno)pyrite (reaction **b**) has a half-time on the order of 20 to 1000 minutes (Stumm and Morgan, 1981). However the regeneration of Fe^{3+} from Fe^{2+} by oxygen (reaction **c**) is essential for the propagation of the overall reaction as direct oxidation of (arseno)pyrite (reactions **a** and **a'**) is quite limited. Reaction **c** is 10^3 to 10^5 times slower (1000

Figure 3.3

After Stumm and Morgan (1981), pg. 470.



Schematic Representation of 3 routes for Pyrite Oxidation
Note: Only 2 (a and a') require oxygen directly

day half-time (Snoeyink and Jenkins, 1980)) than the opposing reduction of the Fe^{3+} by the pyritic mineral (reaction **b**). At higher pH (≥4) the rate of ferrous oxidation increases, however considering the amount of H^+ produced by the oxidation of arsenopyrite (similar to acid mine drainage) and the low buffering capacity of the tailings (alkalinity = 17 mg/L as $CaCO_3$ (analysis by NorWest Labs, sample taken July 17, 1989)), the pH could be expected to drop quite quickly, inhibiting the iron oxidation step. Apparently, therefore, from a chemical viewpoint, mineral oxidation, in the absence of an external source of Fe^{3+}, should be quite slow and arsenic leaching should be insignificant from that source.

3.6.3.2 Precipitate

In oxidizing conditions the Ferri-Floc treatment precipitate is thermodynamically stable. The longterm stability of these arsenic bearing precipitates has been well studied in recent years. Robins (1985, 1988) and Robins et al. (1988) suggest that goethite (FeOOH) is the slightly thermodynamically favoured iron oxyhydroxide, hence the difference between Figures 3.1 and 3.2. Goethite is the result of ageing and is the anhydrous, crystallized, version of $Fe(OH)_3$. Goethite has considerably less adsorptive capacity than the amorphous precipitate. However, studies have shown that the transformation is very slow. Kraus and Ettel (1988) found no significant release of arsenic after two years. Robins et al. are examining the inhibiting effects on ageing of both arsenate and sulphate as well as the accelerating effects of humics, surfactants, silica particles, etc. (Robins et al., 1988).

Kraus and Ettel (1985, 1987) have shown that Fe-As precipitates formed from 0.1M solutions at pH 5 at 25°C and 80°C to have Fe/As=17.1 and be resistant to leaching at up to pH 8 for two years. Harris and Monette (1988) similarly found precipitates with Fe/As=5.5 resistant to leaching (dissolved As<0.5 mg/L) at pH 6.9, over the test duration of 113 days. Harris and Monette's precipitate was formed at pH 8 and was leached at a solid to liquid ratio of 16:1.

3.6.4 Kinetics of Microbial Leaching

3.6.4.1 Mineral

Microbially mediated leaching of arsenic bearing minerals is extremely rapid in comparison to simple chemical leaching. This is because the microorganisms catalyze the oxidation of the ferrous ion back to ferric ion thus eliminating that stage as the rate determining step. The organisms responsible are members of the genera *Thiobacillus* (sulphur) and *Ferrobacillus* (iron). Two of the species that have been tested specifically are *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans*. Studies on bacterial action involved in acid mine drainage have shown that the rate of ferrous oxidation to be 10^6 times greater when microbially catalyzed than when simply chemically mediated (Snoeyink and Jenkins, 1980).

In 1964, Ehrlich tested *Thiobacillus ferrooxidans* TM on arsenopyrite and found that after 21 days at 30°C and 60:1 liquid to solid ratio, arsenic concentrations were twice as high with bacteria present, as without. This represented 18% of the total arsenic present. The arsenic was found to have solublized both as arsenite and arsenate (Ehrlich, 1964). As part of a study by

Kamalov et al. in 1973, a carbonaceous gold ore containing 6% arsenic was leached by *T. ferrooxidans*, releasing 90% of the arsenic present, in just 10 days (reported by Ehrlich, 1981). As well, studies by Polkin and Tanzhnyanskaya in 1968 and Pol'kin et al. in 1973 showed that *Thiobacillus* accelerated, by a factor of 7, the leaching of arsenic from finely divided arsenopyrite (reported in Ehrlich, 1981).

3.6.4.2 Precipitate

Studies on ferric hydroxide precipitates have been less explicit, because of the multitude of co-precipitants available in natural systems. Arsenic releases have occurred under both aerobic and anaerobic conditions, with higher releases in reducing conditions. Mok and Wai (1989) leached creek sediment for 10 days at room temperature at a 13.3:1 L/S ratio. Deuel and Swoboda (1972) incubated soil at 38°C for 1 to 4 weeks, and added sugar to achieve mildly reducing conditions (E_H= +40 to +100 mV). Mok and Wai, and Deuel and Swoboda, both attribute the arsenic releases to the reduction of the ferric ion to ferrous, which is more soluble. The arsenic was adsorbed originally as arsenate (which adsorbs preferentially over arsenite (Pierce and Moore, 1982)) and consequently is released as arsenate. Apparently, there is little reduction of the arsenic. Under anaerobic conditions Mok and Wai leached 3.200 µg As/g sediment as As(V) and only 0.050 µg/g as As(III) in 240 hours. This represented over 7% of the total arsenic present, from a sediment with an Fe/As ratio of 615:1. Lupin precipitate contains approximately 40 mg As/g of sediment (at an Fe/As ratio of 18:1).

A recent study by Francis and Dodge (1990) confirms that the (bacterial) reduction of iron is the release mechanism for a variety of heavy metals

co-precipitated with iron. However, they do mention that the net release of precipitated metal is dependent on a wide variety of geochemical interactions.

Brannon and Patrick (1987) have shown that a natural sediment spiked (after two weeks of equilibration at 28°C) with sodium arsenate, and having an Fe/As ratio of 21:1, will release 50-70% of the arsenic at low pH (5.0 and 6.5) under reducing conditions (E_h= -150 mV), and 20% of the arsenic at pH 8 and E_h= +500 mV, after 45 days of incubation at 20°C. In the case of the strong reducing conditions, the arsenic is released as arsenite (As(III)). This does not necessarily contradict the conclusions of Deuel and Swoboda and Mok and Wai since Brannon and Patrick have imposed more severe conditions and allowed more time. Deuel and Swoboda allowed 4 weeks and only achieved an E_h= +100 mV, Mok and Wai leached for only 10 days. The release of arsenic at high pH and high E_h is probably due to desorption of the arsenic rather than solubilization of the ferric hydroxide precipitate (Brannon and Patrick, 1987). All three groups of experimenters were using natural sediments or soils with ubiquitous bacterial species. No additional bacteria were supplied.

In addition, Pierce and Moore (1982) have shown that arsenic adsorbed after the iron precipitation does not bond as strongly as arsenic adsorbed concurrently with precipitation (co-precipitation). Thus the data of Brannon and Patrick should be taken as levels of maximum leaching, not as typical values.

3.6.5 Method for Chemical Extraction (Leaching)

Evaluation of leachability of a solid is a complex task. It is virtually impossible to simulate all of the natural variables in the laboratory. The

Wastewater Technology Centre in Burlington, Ontario has produced a compendium of leach tests which is the source of most of the paragraph below (WTC, 1989).

The traditional leach test, recommended by the US EPA, is a simple batch extraction with pH adjusted distilled water. This led to the development of the sequential chemical extraction test in which a variety of chemical leachants are used to determine into which phase the contaminants will partition. Some of the leach media used are: water containing 1 M LiCl/CsCl salts, 1 M sodium acetate buffered with acetic acid to pH 5, hydoxylamine hydrochloride in acetic acid, 30% hydrogen peroxide in dilute nitric acid and finally hydrofluoric acid with aqua regia (Bridle et al., 1987). These help simulate a variety of reduction/oxidation and pH conditions which should allow the investigator a greater chance of determining the most likely conditions under which the contaminants will dissolve. Since the waste at Lupin is comparatively well characterized, this is not overly important as solubility conditions can be estimated from the thermodynamic stability regions of the waste.

4.0 METHODS AND METHOD DEVELOPMENT

4.1 Arsenic Speciation

4.1.1 Analytical Method Selected for Total Arsenic

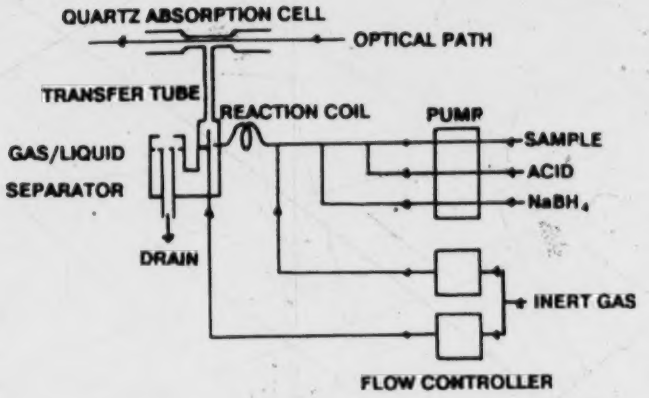
As the equipment available at Lupin consisted of a Varian AA-1275 atomic absorption spectrophotometer with hollow cathode lamps, and a Varian VGA-76 continuous vapour generation accessory, the obvious choice of method was that of continuous hydride generation. The procedure followed is basically that suggested by Varian in a brochure by Brodie et al. (1983). Figure 4.1 gives a schematic of the hydride generation process. Solution is withdrawn simultaneously from the acid and borohydride containers and the sample test tube. First the acid and sample flows are combined, then this stream is mixed thoroughly with the borohydride in a reaction coil. Then the mixture is introduced to a gas/liquid separator (Figure 4.2) where the liquid phase goes to waste and the vapour phase containing nitrogen, hydrogen and arsine is mixed with fresh nitrogen (to ensure the vapour stream is not saturated with water vapour) and transported through a short rubber tube to the quartz atomisation cell. Table 4.1 contains a list of all of the reagents used in this project, including manufacturer and product specifications.

The AA itself was set up with the operational parameters given in Table 4.2. These were selected primarily because they were already used at Lupin and as there was no obvious reason to choose any other conditions, preliminary confirmation of their suitability was made. The response time

Figure 4.1

Schematic of the Vapour Generation Accessory

After: Brodie et al., 1983



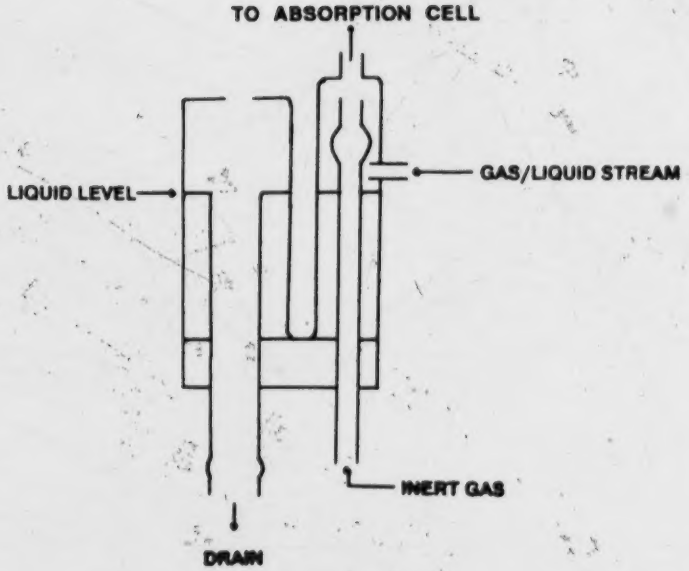


Figure 4.2

Schematic of the Gas/Liquid Separator

After: Brodie et al., 1983

Table 4.1

Reagents Used in this Study

Chemical	Manufacturer	Grade
Sodium arsenite $NaAsO_2$	Fisher Scientific	Reagent Grade
Arsenic trioxide As_2O_3		
Sodium arsenate dibasic heptahydrate $Na_2HAsO_4 \cdot 7H_2O$	Baker	Analyzed Reagent 101.2% purity by iodometry
Sodium borohydride $NaBH_4$	Caledon	95%
Potassium iodide KI	Fisher	ACS specifications
Sodium hydroxide NaOH	Fisher	ACS
Nitric Acid HNO_3	Van Waters & Rogers	ACS
Hydrochloric acid HCl	Fisher	ACS

Table 4.2

AAS Operating Conditions

Wavelength	193.7 nm
Slit Width	1.0 nm
Lamp Current	5 mA
Deuterium Background Correction	On
Acetylene Flow Rate	1.8 L/min
Air Flow Rate	5.5 L/min
Integration Time	3 seconds

(signal rise time) was about 20 seconds, so a delay time of 30 seconds was allowed to ensure a stable signal. A signal integration period of 3 seconds was selected, as this was the time allowed by Brodie et al. (1983). Similar work by Lepla (1989) at Sherrit-Gordon used a 5 second integration period.

In both this project and at Sherrit-Gordon the signal was monitored continuously for 30 seconds (10 readings at Lupin). Brodie et al. took only 3 consecutive readings.

The operating parameters for the continous hydride generator are presented in Table 4.3. The variability of the flow rates may have caused some irrelevant, between day, variations in absorbance readings, but had little

effect on absorbance during a particular run. The worst case would be a change in arsenic concentration of 5%, however, flow rates were measured before and after each sample run and calculated variations in concentration was usually less than 2% (which is quite small considering the overall accuracy of the procedure).

There are some differences between Brodie et al.'s analytical procedure and the method used for this work. Brodie et al. used HCl at 10 M in the acid channel while at Lupin concentrated HCl (11-12M) was used, to minimize acid handling. The only important consideration, with regard to the acid concentration, seems to be that the pH in the reaction tubing be at or below pH 1 (APHA-AWWA-WPCF, 1985), although Arbab-Zavar and Howard (1980) report increasing arsenic (V) recovery until at least 3 M HCl was used ($p^cH < -0.5$). The sample preparation process reported by Brodie et al. suggests a 50 minute reduction using a 1% w/v potassium iodide solution. However studies early in the project indicated that a reduction time of at least 3 hours was necessary to minimize reduction time as a variable in measured absorbance. Figure 4.3 shows how the absorbance readings of a set of standards asymptotically approach maximum values. Heating the samples to 60-70°C helped accelerate the reduction process. Brodie et al. reported only 20% response from unreduced samples of As(V) compared to similar concentrations of As(III). Figure 4.3 indicates initial response of 20 - 25% of full signal strength. For work at Lupin, dilution of the reductant by the sample was limited to 18% (i.e. 15 mL of sample into 85 mL of KI solution for the 15µg/L standard), usually dilution was closer to 1% although 11% was often selected.

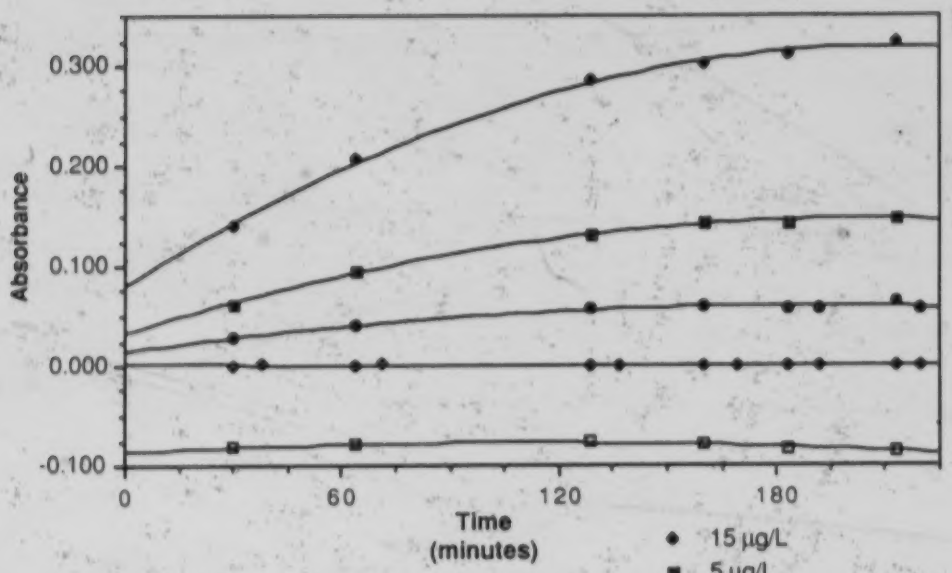
Table 4.3

Hydride Generator Operating Specifications

Sample Flow Rate	7-8 mL/min
Acid Flow Rate	0.9-1.1 mL/min
Borohydride Flow Rate	0.9-1.1 mL/min
Rinse Time	10 seconds

Figure 4.3

Time Dependency of As(V) Reduction



Note: All standards contained 2 µg/L As(III)

The selected methodolgy facilitated analysis of around 25 samples in a fourteen hour day, as long as the right levels of dilution had been previously determined. Initial dilution was made with deionized distilled water with glass pipets and volumetric flasks, having an accuracy of 99.9%, no replicate dilutions were made, as this degree of variability was deemed insignificant (although the accuracy of the glassware does not preclude the possibility of operator error). All samples were diluted into test tubes with KI solution, in duplicate, as this stage was done by autopipet, which was accurate to +/-2%. Dilution of up to 200 fold was possible directly into the test tube (0.1 mL of sample diluted to 20 mL with KI solution).

4.1.2 Statistical Aspects of Total Arsenic Determination

After the system had been conditioned by alternately presenting the highest standard and blank until the signal stabilized, the calibration standards were run. Ten readings of the measured absorbance were recorded for each concentration. The mean absorbance was calculated, as was the variance of the readings. A calibration curve was prepared by plotting the mean absorbances against the 'true' concentrations of the standards. A quadratic regression line was fit through the data points by the method of linear least squares (regression equation is linear in the coefficients). The variances of the absorbances were pooled using the formula:

$$s^2 = \frac{(n_1-1)s_1^2 + (n_2-1)s_2^2 + (n_3-1)s_3^2 + \text{etc.}}{n_1 + n_2 + n_3 + \text{etc.} - \#\text{ of calibration standards}}$$

where s is the standard deviation of the absorbance readings at each concentration and n is the number of absorbance readings taken at each

concentration. The variances were then tested using Bartlett's special application of the X^2 test to ensure that they were all, in fact, the same, and hence came from the same population (Kennedy and Neville, 1976). Once the variance had been determined it was possible to establish the 95% confidence limits for the regression line. This confidence interval was used to calculate a confidence interval in terms of concentration for each sample from the regression equation, using the mean absorbance of the sample. Again Bartlett's test was used to verify that the variance of the sample absorbances was the same as the (pooled) variance of the calibration standards.

4.1.3 Method Selected for Arsenic (III) Determination

The method selected for arsenic (III) determination is essentially unchanged from the method used for arsenic (V). The main differences lie in the absence of a pre-reduction stage, and the inclusion of careful pH control with a sodium acetate-acetic acid buffer (replacing the acid stream). Eliminating the pre-reduction stage saves considerable time in the preparation of samples as all dilutions are made using deionised distilled water and no reduction time needs to be allowed for. The easiest way of determining buffering success was to measure the pH of the liquid waste from the gas/liquid separation vessel.

Various acetate concentrations were tested to try and locate an optimum value to maximize signal strength while minimizing the signal to noise (S/N) ratio. Initial results showed extreme response suppression at high acetate concentrations compared to analyses of arsenic (III) solutions

made with concentrated HCl. This is believed to be caused by poor gas/liquid (G/L) separation because of the high viscosity of the liquid phase.

The effects of various borohydride and acetate concentrations on waste pH and signal strength were examined. The most important trend was the decreased S/N ratio with increasing borohydride concentration, despite a concomitant increase in signal strength. This corresponded to an increase in bubbling, frothing and bumping in the G/L separator with consequent entrainment of liquid into the arsine transfer tube. Secondly was the increase in waste pH at low acetate concentration (i.e. the buffer capacity was exceeded by the basic borohydride solution), which was especially evident at or below 0.5 M acetate. Although the pH of the buffer itself was not usually varied, some preliminary work in this area indicated that this was not a contributing factor compared to buffer concentration. The ratio of salt concentration to acid concentration was usually 0.294 Molar/0.699 Molar or 0.42:1, which gives a calculated pH 4.3, which was measured as pH 4.2 (because of the high ionic strength of the buffer solution). The measured pH of the waste was usually around pH 5.0. Studies showed that the inhibition in response was more pronounced from using higher strength buffers than from allowing the pH of the reaction to increase, as long as the pH remained below about pH 5.8.

Eventually a buffer strength of 1 M acetate was chosen. This was prepared from 20 mL of glacial acetic acid (Fischer ACS grade) and 20 g of sodium acetate trihydrate diluted to 500 mL with deionised distilled water. To minimize the effect of the NaOH preservative in the borohydride solution, only 4 g/L NaOH was used, as compared to the 8 g/L recommended

in the literature (APHA-AWWA-WPCF, 1989). Fresh borohydride solution was prepared daily.

The borohydride solution strength was selected to be 1%, based on results which showed that that concentration gave the highest response with a 10 µg/L solution of As(III) reacted with concentrated HCl. Figure 4.4 illustrates these results from Lupin. Figure 4.5 is taken from a study on selenium by Ek and Huldén (1987) for which the same results hold true. A contributing factor was the excess back pressure in the system caused by the hydrogen gas which was unable to escape quickly enough, resulting in burst seals, at high levels of borohydride.

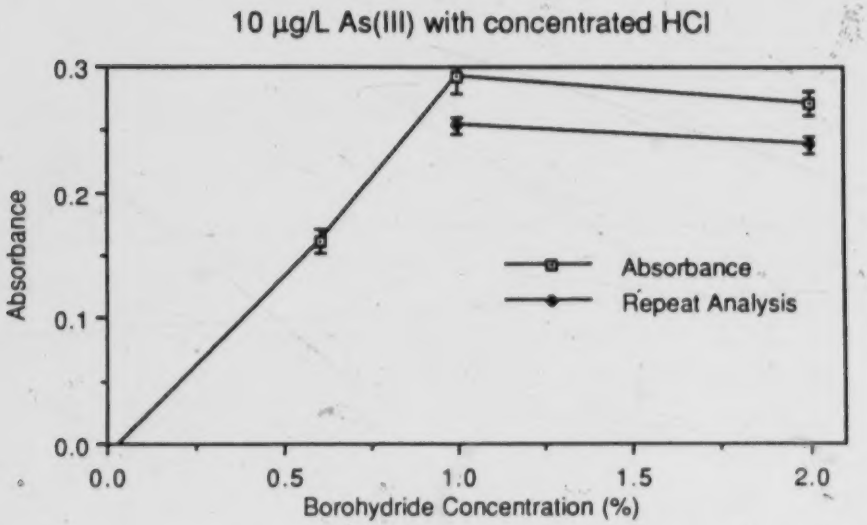
AA response of As(III) from the buffered solution compared to hydride generated from addition of concentrated HCl was generally about one third lower (i.e. 15 µg/L of As(III) at pH 5 gave the same absorbance as 10 µg/L of As(III) at pH -1). It is suspected that this is because of the diminished availability of hydrogen ions at pH 5 (compared to pH 0 for As(V) determination), resulting in restricted production of hydrogen radicals.

4.1.4 Statistical Aspects of Arsenic (III) Determination

Although the procedures for statistical analysis are the same as for total arsenic, two important points must be remembered when analyzing for arsenic (III). The greatly increased detection limit (close to 2 µg/L), caused by the uneven bubbling in the gas/liquid separator, dramatically increases the uncertainty in measurement of arsenic concentration. Combine this with the depressed absorbance response which exists in arsenic (III) measurement, compared with total arsenic analysis, and it becomes very apparent that it is

Figure 4.4

Absorbance Response versus Borohydride Concentration



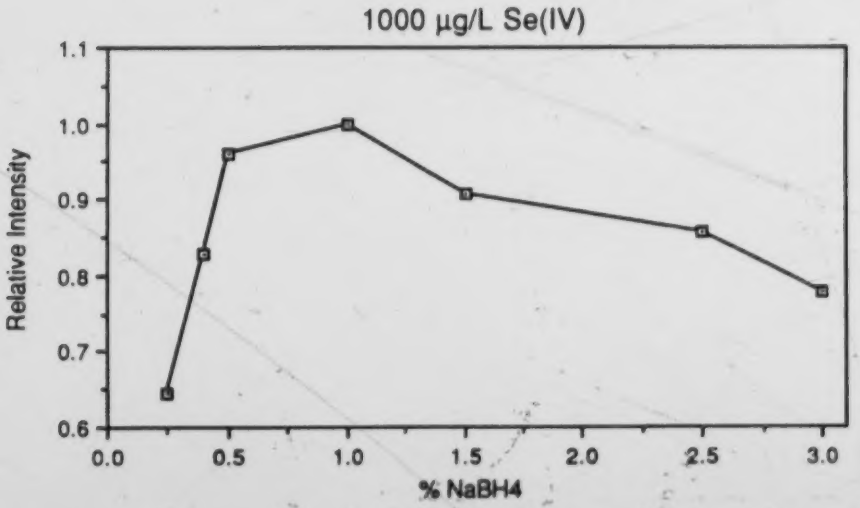


Figure 4.5

Absorbance Response versus Borohydride Concentration (for Selenium)
After Ek and Huldén, 1987

essential to operate at much higher concentrations than would be appropriate for total arsenic determination.

The deviation from linearity of the calibration curve appeared to be a function of the absorbance (response) rather than concentration of the arsenic in the standards. For arsenic (III) determination the deviation from linearity does not become significant until the concentration is greater than 15 μg/L. This helps reduce the contribution to the uncertainty in measurement from this source. Ideally the optimum region for analysis would be at concentrations at least an order of magnitude greater than the detection limit, to minimize the error from the background noise. This is not possible with this method as it stands now. This will be discussed further in Chapter 5.

4.2 Bioassay Methods

To evaluate the acute lethality of arsenic on rainbow trout, it was necessary to spike the water from Lupin's Pond 2 with high levels of arsenic (III) and arsenic (V). In the July bioassay, nine 20 litre plastic water jugs were filled with water from the surface of Pond 2 at sample location 102. Three jugs were left unadulterated, as controls. Three were spiked with 1.00 g each of sodium arsenite ($NaAsO_2$) (Fischer Chemical, ACS analytical grade) which is equivalent to 28.8 mg As(III)/L. The remaining three were spiked with 5.00 g each of sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) (Baker Analyzed Reagent, 0.01% arsenite), which is equivalent to 60 mg As(V)/L. For the August bioassay, three containers were spiked with 1.60 g of sodium arsenite giving an As(III) concentration of 46 mg/L. Three more containers were spiked with 8.0 g of sodium arsenate for an As(V) concentration of 96 mg/L. Again three

containers were left unspiked, to facilitate estimation of the effects of the other toxicants in Pond 2 water.

After the water had been treated with arsenic it was shipped by air to Edmonton where the bioassays were started, within 48 hours of sampling, by Chemical and Geological Laboratories. There the water was diluted by 0%, 20%, 40%, 60% and 80% into 22 L rigid plastic containers with disposable plastic linings, to give a working volume of 20 L. Ten fingerlings with an average weight of 1 g and an average length of 3 cm were added to each container. This gave an organism loading rate of 0.5 g/L. The tests were run for 96 hours at 15°C. The dilution water used was Edmonton tap water, typical specifications of which are given in Table 4.3. The water was dechlorinated with activated carbon. The major chemical characteristics of the Pond 2 water were determined by NorWest Labs in Edmonton. These data are also included in Table 4.3.

4.3 Jar Tests

4.3.1 Experimental Design for Jar Testing

As the purpose of the jar tests was to imitate actual operating conditions, it was decided to choose mixing conditions (combinations of mixing time and intensity) which would approximate initial and final mix conditions. This was an obvious starting point for a bi-level design. The centre point would then correspond to the mid-level operating conditions of the syphons. The flow in the syphons is dependent on the head between the

Table 4.3.

Water Quality for Bioassays

Water Quality Parameter	Edmonton Tap Water July	Edmonton Tap Water August	Pond 2 July	Pond 2 August
Cations				
Hardness (mg/L as $CaCO_3$)	114	116	136	141
Calcium	28.8	30.4	51.2	51.7
Magnesium	10.2	9.72	2.0	2.8
Sodium	6.8	4.13	135	132
Potassium	2.61	0.73	7.3	7.0
Iron	0.002	0.011	1.03	0.76
Zinc	<0.001	0.007	0.127	0.180
Anions				
Alkalinity (mg/L as $CaCO_3$)	48	48	17	10
Arsenic (mg/L as As)	0.0003	n/a	0.360	0.320
Cyanide	<0.001	<0.001	0.390	0.057
Bicarbonate	56.7	56.7	20.9	11.6
Sulphate	63	65	293	341
Chloride	2.83	1.71	79.1	96.0
Other Parameters				
pH	8.0	8.1	7.1	6.6
Total Organic Carbon	3.21	3.30	3.5	n/a

All Water Quality Parameters except pH are in units of mg/L .
(n/a - not available)

Sources: City of Edmonton Monthly Water Quality Summary Report July and August, 1989; NorWest Labs - independent analysis of Pond 2 water

ends of the pipe. The flow and energy imparted to the water (as well as the rate at which that energy is imparted) all vary as the level of Pond 1 drops and that of Pond 2 rises.

In order to determine if the dose could be lowered any further (it has been lowered year after year to its 1989 target level of 12:1 Fe/As mole ratio), the two-level design was used with the current dose as the high level. The low end was selected based on literature discussion which indicated that Fe/As of 4:1 was less than the minimum for acceptable removal (Kraus and Ettel, 1987; Harris and Monette, 1988). This was to ensure measureable change in arsenic concentration as a result of variation in dosage.

Thus the final experimental design was a 2^3 factorial design. The variables were dose and Gt values for rapid mix and flocculation. The discussion for the estimation of appropriate Gt values is presented below. The assumptions common to all of the calculations were: constant water temperature at 10°C with its associated physical properties of density and viscosity, g = 9.8 m/s^2, Schedule 100 pipe used (whether steel or polyethylene) to ensure constant inside diameter, initial head of 2.88 m, final head of 0.43 m, initial flow rate of 0.49 m^3/s and a final flow rate of 0.20 m^3/s. The variables were based primarily on 1988 flow conditions although some were corrected for known 1989 values (e.g., initial head)).

4.3.2 Coagulation (Rapid Mix)

Rapid mix was assumed to occur in the narrow part of the syphons, between the intake and outfall sections, above the two waterlines, as

illustrated in Figure 4.6. This gave an approximate mixing length of 32 m, for a mixing volume of 4.9 m^3. The G value can be calculated from

$$G=(Q\rho gh/V\mu)^{1/2}$$

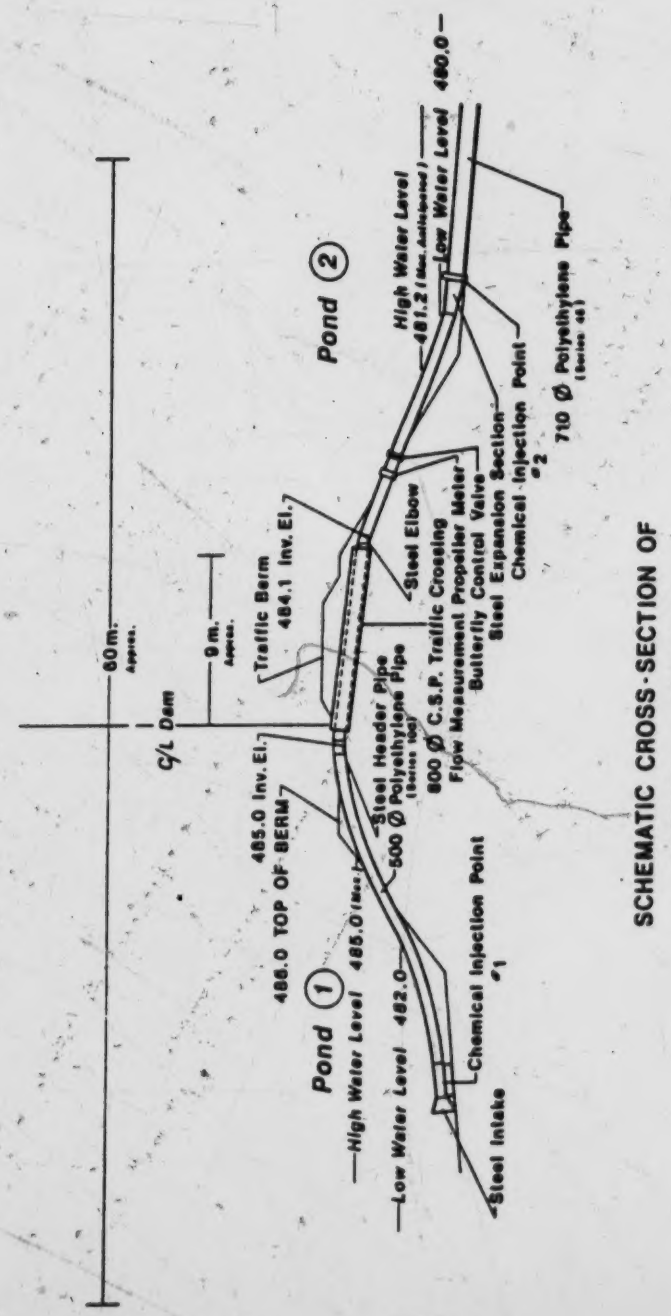
where:

Q is the initial volumetric flow rate through the syphon,
ρ is the density of the water,
g is the gravitational constant,
h is the head,
V is the volume contained within the syphon and
μ is the viscosity of the water;

which gives a G = 1465/s at the initial operating conditions. The residence time, t = V/Q, is 10 seconds. This G value corresponds to a very high impeller speed of ~520 rpm in the jar tester (Cornell and Bishop, 1983). However, equipment limitations restrict jar tester operation to a maximum of 100 rpm. Consequently the scale down correlation for rapid mix was made with respect to the total power imparted, Gt, not simply G. So to achieve a value of Gt = 14650 with G at 100 rpm of 100/s, it becomes necessary to mix for 148 seconds. A similar problem existed for rapid mix at the final operating conditions. Full scale conditions had G = 362/s (or 200 rpm in the jar tester) and t = 24.6 seconds for a Gt = 8905. On a lab scale this was correlated to G = 100/s (100 rpm) and t = 89 sec.

Since coagulation only requires a few seconds at most, it was felt that these rapid mix times would probably be detrimental to the flocs (Lang et al., 1988), however little can be done to the syphons to reduce the magnitude of the high intensity mixing. The rapid mix part of this experiment had little direct physical correspondance to the actual conditions in the syphons. However, it should provide an approximation of the rapid mix produced by the syphons.

Figure 4.6
Source: Wilson (1989a)



4.3.3 Flocculation

Flocculation was assumed to begin as soon as the syphons widen into the discharge zone. The nominal pipe diameter increases to 710 mm resulting in a decrease in water velocity. It was felt that the flocculation could be broken into three stages; the initial high intensity phase in the discharge portion of the syphon, the turbulent portion of Pond 2 in the vicinity of the syphons and finally the gentle mixing caused by wind action on the pond. The second and third stages could be augmented by the installation of mechanical flocculators near the discharge from the syphons.

The main difficulty in trying to approximate the degree of mixing lies in estimating the period of time over which the kinetic energy of the water, from the syphons, is dissipated. This led to the concept of modelling the flocculation by a three stage tapered flocculator which could then be simulated with the jar tester. To minimize the variables the mixing time at only one mixer speed was varied. The first stage of flocculation is at 80 rpm, which coincidentally corresponds to the G value in the syphon discharge at the end of the treatment run. Mixing at 80 rpm was for 20 seconds. The second flocculation stage, which is to represent either a dissapation stage from the syphon or turbulent mixing in the pond, was at 50 rpm. The centre-point was selected to be 9 minutes with low and high values of 3 and 15 minutes respectively. The third stage was at 20 rpm, to represent the slow turning of the water in the pond because of wind action, this was for a 15 minute period.

4.3.4 Summary

In summary the operationing conditions for the jar test experiments were as follows:

Control Parameter	+1	-1	Centrepoint
Dose	12:1	4:1	8:1
Rapid Mix (100 rpm)	200 seconds	80 seconds	140 seconds
Floc mix (80 rpm)	20 sec	20 sec	20 sec
" " (50 rpm)	15 minutes	3 minutes	9 minutes
" " (20 rpm)	15 min	15 min	15 min

A second set of experiments was performed after the results for the first set had been analysed. The operating conditions were then as follows:

Control Parameter	+1	-1	Centrepoint
Dose	24:1	12:1	16:1
Rapid Mix (100 rpm)	80 seconds	80 seconds	80 seconds
Floc mix (80 rpm)	20 sec	20 sec	20 sec
" " (50 rpm)	9 minutes	1 minutes	5 minutes
" " (20 rpm)	0 min	0 min	0 min

For both experimental sets the floc was allowed to settle for 10 minutes before sampling from the mid-depth tap. Arsenic concentration in the decant was the only measured variable.

4.4 Measurement of Arsenic in Inorganic Solids

4.4.1 Estimation of Total Recoverable Arsenic

The measurement of the arsenic content of solid materials requires the dissolution of arsenic into water. To facilitate determination of the total amount of arsenic present, concentrated acids are used. Aqua regia (3 parts HCl to 1 part HNO_3) has often been used (Mok and Wai, 1989; Abernathy, et al., 1984; Agemain and Bedek, 1980) as the leachant. Other researchers have made use of perchloric acid because of its powerful oxidizing properties (Agemain and Bedek, 1980). It was not felt that this was required for arsenic since it is usually used for selenium, which is soluble only under highly oxidizing conditions. In addition, the laboratory at Lupin was not equipped with fumehoods capable of handling the fumes produced from perchloric digestion.

Some preliminary work indicated a need to use a high liquid to solid ratio and 40:1 was eventually selected as an adequate level (higher levels were tried but there was no incremental recovery). All leaches were run in triplicate, with duplicate blanks, however no attempt was made to evaluate % recovery, beyond establishing the minimum L/S ratio. The high correspondence between results obtained at Lupin and independently by Baum (1988) and Lakefield (1988) was deemed sufficient validation.

Sample and acid were mixed in an Erlenmeyer flask and then boiled for two hours. After cooling to room temperature the leachate was filtered through Whatman GF/C glass fibre filter paper. The filtrate was diluted to a known volume in a volumetric flask and the arsenic content was determined

as described in Section 4.1.1. The mean absorbance of the blanks was subtracted from the measured absorbance of the triplicate samples before the concentration was calculated from the calibration curve regression equation.

4.4.2 Leachable Arsenic Determination

There are many controllable variables in leach tests. The main ones are leach contact time, leach temperature, leachant composition, liquid to solid ratio, sample preparation, and method of contact. The method of contact can be sub-classified as to whether the leach solution is added only once and left in contact for the entire test duration (batch extraction), renewed at regular intervals (sequential batch), or if it flows through the solid media for only a single contact (continuous flow). All three are in common use, the latter two are dynamic tests. There are ASTM standard methods for each of the three contact methods. The U.S. EPA (reported in WTC, 1989) recommends an agitated batch test with a short contact period. The standard U.S. EPA leach test uses a pH 5.5 solution containing acetic acid which is commonly replaced with sulphuric acid for industrial wastes.

The procedure followed for this work was similar to that recommended for the modified U.S. EPA leach test. A liquid to solid ratio of 20:1 was used, with deionised distilled water as the solvent. No pH adjustment was made, as the natural system will have little buffering capacity. The test was not intended to reflect site specific conditions, however, the final pH will reflect the interaction of the leachant (deionised water) with the buffering capacity of the solids (WTC, 1989). Covered, but not sealed, Erlenmeyer flasks were placed on a shaker table to help maintain oxygenated and potentially acidic conditions. ASTM Method D3987-85 recommends a 29

rpm shaker speed, however, because of the high specific gravity of the solids in this study (high iron content), a shaker speed of approximately 100 rpm was used to ensure the solids were well contacted by the liquid. The leach time used was 4 days rather than the the more common 18 to 48 hours (ASTM and EPA (in WTC, 1989), respectively), to facilitate closer approach to equilibrium conditions. The leachate was separated from the solids by vacuum fitration through Whatman glass fibre 0.45µ filter paper and then analyzed as described in Section 4.1.1.

Triplicate samples of both the mineral tails solids and the treatment precipitate were leached, each with duplicate blanks. Approximately 5 grams of tails solids and 1 gram of precipitate, respectively, were used.

5.0 RESULTS AND DISCUSSION

5.1 Arsenic Speciation

The measurement of the total arsenic content of water is a relatively simple task with a continuous hydride generator. Many sampling runs were made over the course of the summer, evaluating the arsenic content at various locations throughout the mill and the tailings basin.

5.1.1 Success of the Total Arsenic Method

Recoveries of U.S. EPA standards varied from a low of 85% to a high of 130%. The EPA reports that the 95% confidence interval on recoveries of their standards gave recoveries from 75.5% to 122%. The confidence limit was defined as twice the standard deviation ($\pm 2\sigma$). Table 5.1 contains the mean recoveries of the standards as determined in this work. The increased mean level of recovery in this work over that predicted by the U.S. EPA is primarily the result of high average recovery of the 0.100 mg/L standard. However the increased recovery is not statistically significant. The standard deviations of the recoveries were all within χ^2 tolerance limits (P=0.05) for representing the same population variance. Table 5.2 summarizes the averages of the recoveries for each 'True Value' (as defined by the U.S. EPA Quality Control Laboratory (1989)) of standard along with the standard deviation. The data provided by the U.S. EPA is included for comparison. The EPA's standard deviation was assumed to be representative of the population standard deviation (σ) while this work is only an approximation, hence is labelled s.

Table 5.1

Recovery of U.S. EPA Standards

True Value (mg/L)	Measured Value (mg/L)	% Recovery	Calibration Curve	Date Analyzed
0.100	0.100	100%	51a	29-Jun
0.100	0.102	102%	51a	29-Jun
0.100	0.088	88%	55b	11-Jul
0.100	0.102	102%	55b	11-Jul
0.100	0.115	115%	55b	11-Jul
0.100	0.104	104%	57c	23-Jul
0.100	0.099	99%	57c	23-Jul
0.100	0.108	108%	59a	24-Jul
0.100	0.108	108%	59a	24-Jul
0.100	0.110	110%	61a	17-Aug
0.100	0.110	110%	61a	17-Aug
0.100	0.107	107%	61c	17-Aug
0.100	0.115	115%	61d	17-Aug
0.100	0.114	114%	63-1a	19-Aug
0.100	0.113	113%	63-3a	19-Aug
0.100	0.114	114%	65-1a	24-Aug
0.100	0.122	122%	65-1c	24-Aug
0.100	0.110	110%	65-1c	24-Aug
0.100	0.110	110%	65-3d	24-Aug
0.100	0.119	119%	67-4a	29-Aug
0.100	0.109	109%	67-4c	29-Aug
0.100	0.116	116%	67-6e	29-Aug
0.100	0.107	107%	69a1	17-Sep
0.100	0.118	118%	69a3	17-Sep
0.100	0.113	113%	73a1	1-Oct
0.100	0.130	130%	73a1	1-Oct
0.100	0.124	124%	73b3	1-Oct
0.100	0.113	113%	73b3	1-Oct

Table 5.1 (continued)

'True' Value (mg/L)	Measured Value (mg/L)	% Recovery	Calibration Curve	Date
0.046	0.044	96%	43c	28-Jun
0.046	0.044	95%	59a	24-Jul
0.046	0.046	99%	61a	17-Aug
0.046	0.046	101%	61f	17-Aug
0.046	0.046	100%	63-1a	19-Aug
0.046	0.046	99%	63-3b	19-Aug
0.046	0.046	99%	65-1a	24-Aug
0.046	0.042	91%	65-1b	24-Aug
0.046	0.045	97%	65-2e	24-Aug
0.046	0.048	105%	67-4a	29-Aug
0.046	0.047	102%	67-4c	29-Aug
0.046	0.046	102%	69a1	17-Sep
0.046	0.053	115%	73a1	1-Oct
0.020	0.017	85%	43a	28-Jun
0.020	0.018	91%	43c	28-Jun
0.020	0.018	92%	55a	8-Jul
0.020	0.019	95%	61a	17-Aug
0.020	0.018	91%	61e	17-Aug
0.020	0.020	102%	63-1a	19-Aug
0.020	0.018	92%	63-3d	19-Aug
0.020	0.020	102%	65-1a	24-Aug
0.020	0.022	108%	65-2e	24-Aug
0.020	0.023	113%	67-4a	29-Aug
0.020	0.024	121%	67-6c	29-Aug
0.020	0.021	106%	69a1	17-Sep
0.020	0.025	125%	73a1	1-Oct

Table 5.2

Recovery of EPA Standards

Concentration of Standard (mg/L)	Average	Standard Deviation (s)	Number of Samples (n)
0.100	110.7%	8.41%	28
EPA 0.100	99.2%	11.00%	
0.046	100.1%	5.72%	13
EPA 0.046	97.8%	10.43%	
0.020	101.8%	12.39%	13
EPA 0.020	98.5%	11.50%	
All	106.0%	10.15%	54
USEPA Regression	99.85%	10.98%	

Source: U.S. EPA Quality Control Laboratory

One recovery value was rejected on the basis of Chauvenet's Test at a 95% confidence level (Kennedy and Neville, 1976), as its % recovery was only 60% (of 0.020 mg/L) while the mean was close to 100% with a 10% standard deviation (Table 5.2). It is difficult to evaluate the recovery of unknown samples and hence reject those with poor recoveries, as they are usually only run in duplicate and an extensive pool of data may not be available. Although the common pond sample points are fairly well characterized, most of the process streams at Lupin are not.

A secondary consideration of the recovery values is the uncertainty in estimating the mean recovery for any given sample of standard. The error from reading the measured concentration of the diluted standard is relatively constant, especially when in the range between the second lowest standard (first standard above the blank) and the second highest standard. The error from this source increases as the deviation from linearity of the calibration

curve increases, as well as at the ends of the regression curve. The contribution to this error because of the dilution is generally less than 1% and often as low as 0.6%, since the error terms are squared in the process of estimating the uncertainty (Holman, 1978). The total percent error is minimized by operating in a calibration range at least 10 times the detection limit. The detection limit is usually less than 0.5 µg/L.

Figure 5.1 illustrates the 95% confidence interval of a typical regression curve. The data points are the measured absorbance values for certain samples as well as the calibration standards. The absorbances and their associated 95% confidence limits for the corresponding concentrations are presented in Table 5.3. Note that the detection limit concentration is calculated from 3σ of the pooled variance of the absorbance (Boumans, 1978), whereas the 95% confidence interval is based on approximately 2s (depending on the number of absorbance readings taken for the sample). The variance of the absorbance readings for each sample is assumed to be the same as the pooled variance of the absorbance readings of the standards, which is also taken as the variance of the blank. For this calibration curve the detection limit is 0.40 µg/L, and the identification limit (6σ) is 0.67 µg/L (Boumans, 1978).

The data presented in Table 5.3 illustrate a number of interesting features of this type of data analysis. The first 6 rows contain the calibration curve data which shows the effect of the error of measuring the absorbance. The 95% confidence interval ranges from ±8% at 2 µg/L to ±3% at 7 and 10 µg/L (calculated from the columns labelled 'minimum' and 'maximum' concentrations). This is a tight interval, compared to other data collected in

Figure 5.1

Typical Regression Curve

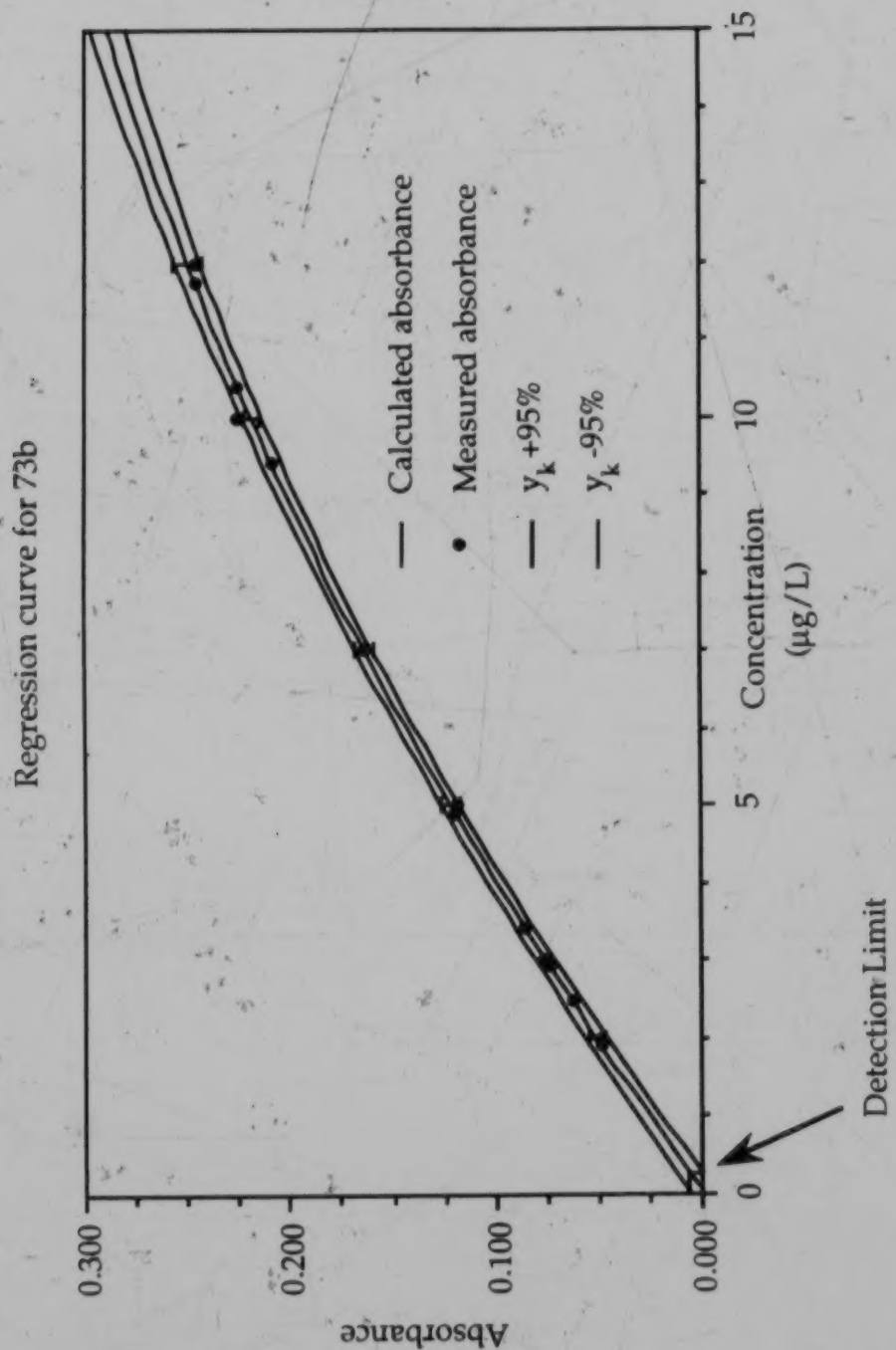


Table 5.3

Typical Results (73b, Oct. 1, 1989)

Sample Label	Mean Absorbance	Mean Concentration (µg/L)	Dilution factor	Mean Concentration (mg/L)	Minimum Concentration * (mg/L)	Maximum Concentration * (mg/L)
0	-0.0020	0.00	1.0	0.000	0.000	0.000
2	0.0506	2.00	50.0	0.100	0.092	0.108
5	0.1216	5.00	20.0	0.100	0.096	0.104
7	0.1635	7.00	14.3	0.100	0.097	0.103
10	0.2184	10.00	10.0	0.100	0.098	0.103
12	0.2497	12.00	8.3	0.100	0.096	0.104
EPA 0.100	0.0626	2.48	50.0	0.124	0.116	0.132
Pond 2 Oct. 1	0.0762	3.04	100.0	0.304	0.286	0.321
EPA 0.100	0.0851	3.41	33.3	0.114	0.108	0.120
Pond 2 Oct. 1	0.0734	2.92	100.0	0.292	0.275	0.309
2 µg/L	0.0489	1.93	50.0	0.097	0.088	0.105
5 µg/L	0.1190	4.88	20.0	0.098	0.094	0.102
7 µg/L	0.1635	7.00	14.3	0.100	0.097	0.103
10 µg/L	0.2250	10.40	10.0	0.104	0.101	0.107
12 µg/L	0.2458	11.74	8.3	0.098	0.094	0.101

* based on 95% confidence limit

this study, which presumably resulted from the 5 second integration time that was used for this particular analysis (Boumans, 1978). The calibration standards were prepared from the 0.100 mg/L daily standard (hence the 0.100 mg/L mean concentration).

The upper limit of the linear range is about 9 μg/L but there is no marked increase in relative error even at 12 μg/L. Error is ±3% at 9 μg/L and ±4% at 12 μg/L which is the result of widening of the regression confidence limits at the ends of the regression line (the confidence limits of regression curves widen at extreme values). Table 5.4 illustrates how the widening of the confidence limits is delayed to higher absorbances by running standards of higher concentration as evidenced by the 15 μg/L standard (the error is still only ±2% at 15 μg/L).

The last 5 lines of Table 5.3 show how the actual measured absorbances of the calibration standards deviate from the regression line. These data points are marked with error bars in Figure 5.1. These absorbance values differ from the first 6 lines of Table 5.3 in that they are the measured data from which the calibration curve was constructed whereas the first 6 lines are simply the calculated absorbances for the given concentration.

In the middle of Table 5.3 are duplicate analyses of the 0.100 mg/L EPA standard, and a sample of water from Pond 2 which was taken on October 1, 1989. The values obtained for the Pond 2 concentration were similar to values obtained in other analyses.

Table 5.4

Typical Results (69a, Sept., 17, 1989)

Sample Label	Mean Absor-bance	Mean Concen-tration (µg/L)	Dilution factor	Mean Concen-tration (mg/L)	Minimum Concen-tration * (mg/L)	Maximum Concen-tration * (mg/L)
0	0.0025	0.00	1.0	0.000	0.000	0.000
5	0.1519	5.00	20.0	0.100	0.097	0.103
7	0.2010	7.00	14.3	0.100	0.098	0.102
10	0.2632	10.00	10.0	0.100	0.098	0.102
12	0.2970	12.00	8.33	0.100	0.098	0.102
15	0.3363	15.00	6.67	0.100	0.098	0.102
20	0.3713	20.00	5.00	0.100	0.092	**
EPA 0.100	0.2756	10.69	10.0	0.107	0.105	0.109
EPA 0.100	0.3601	17.72	6.67	0.118	0.114	0.124
EPA 0.046	0.1441	4.70	10.0	0.047	0.046	0.048
EPA 0.020	0.0706	2.12	10.0	0.021	0.020	0.023
Pond 1 Sept. 14	0.1503	4.94	500	2.47	2.40	2.54
Pond 1 Sept. 16	0.1540	5.08	500	2.54	2.47	2.61
Tails Solution July 21	0.2420	8.900	2000	17.8	17.4	18.2
Pond 1 Aug. 27	0.3222	13.80	200	2.76	2.70	2.82
Pond 1 Aug. 28	0.3236	14.32	200	2.86	2.80	2.93

* based on the 95% confidence limit

** Upper confidence limit is out of the calibration range

The limits of the 95% confidence interval for each analysis were within 6% of the mean concentration. Both means lay within the 95% confidence interval of the other sample. Thus this sample of Pond 2 water could be said to contain an average value of 0.30 mg/L ±6% (0.02 mg/L) of total arsenic, or that it is 95% certain that the arsenic concentration of that sample of Pond 2 water lies between 0.28 and 0.32 mg/L. In order to evaluate the statistical significance of the contribution from the error in diluting the sample, it would be necessary to perform many repeat dilutions. The proximity of the two concentrations exhibits the expected good reproducibility of the dilution (high precision), as these two values deviate only 2% from their average.

One aspect of the method that has not been investigated thoroughly is the potential presence of interferences. Interfering ions can cause either over- or under-estimation of the arsenic concentration. Usually they cause a suppression in the response and hence an under-estimation of the amount of arsenic present.

It is believed that the concentration of the usual interfering compounds (Cu, Ni, Fe) is too low to be of importance, especially with the levels of dilution commonly used with this method for water samples at Lupin. Yamamoto, et al. (1981) suggest that, at worst, copper levels would have to be 600 times greater than arsenic levels to cause 10% suppression of response, whereas at Lupin the levels are quite similar to each other (i.e., within one order of magnitude).

Ideally each major process stream and the tailings ponds should be sampled and analysed by the method of standard additions. This method implies that the added analyte will behave identically to the existing, as yet

unquantified, analyte (Welz, 1986). The calibration curve should be prepared from equally spaced standards (e.g., 0, 3, 6, 9,12 and 15 µg/L) and then the sample should be diluted so that the diluted concentration is approximately equal to the separation between the standards (i.e., 3 µg/L) then appropriate amounts of standard should be added to a series of the diluted sample and a new calibration curve prepared. If the two calibration curves parallel each other, there are no interferences. If there is evidence of interference, the second calibration curve will have to extrapolated to the x-axis and the absolute value of the x-intercept taken to be the value of the concentration. It must be remembered that the confidence interval widens towards the ends of the regression curve and, in this case, the curve is being extrapolated, thus the range of possible values can become quite large. There are a number of papers on this subject. The reader is referred to Franke, et al., (1978), Saxberg and Kowalski (1979), and Welz (1986) for excellent discussions on the method and its drawbacks.

Because of the difficulty in estimating the unknown concentration to which the standard was added, the data generated were never quite in the ideal range described above. Either there was too little unknown thus creating a suspision that the interferences were unobservably small (i.e., only the standard was being measured) or there was too much unknown (i.e., insufficient standard was added) and the confidence in the extrapolated calibration line was unreasonably low. The end result is that there is insufficient data to say with certainty whether there is or is not any interferences with the method of total arsenic determination used in this work.

5.1.2 Measurement of Arsenic (III) Concentration

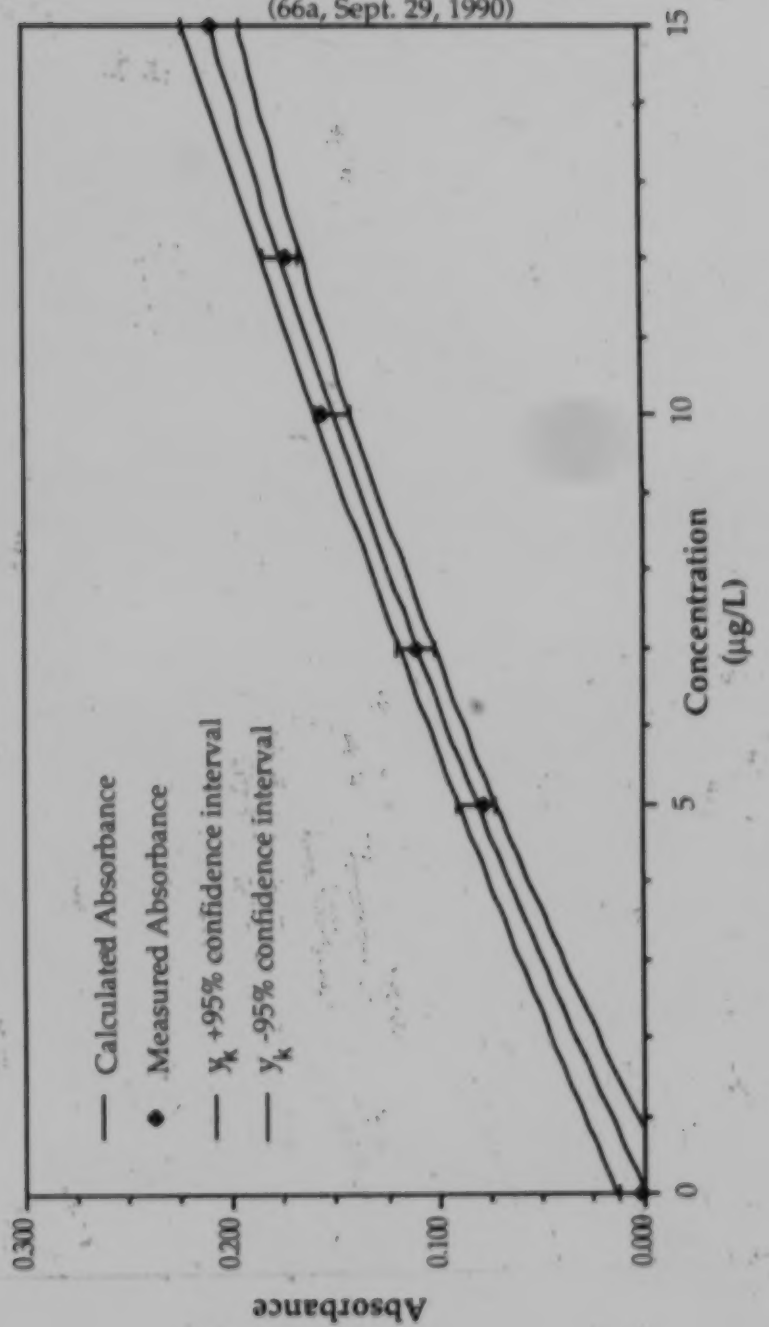
Although the method is quite simple in principle, a number of operational difficulties still need to be overcome. The main problems remaining are the slight recovery of As(V) at high As(V)/As(III) ratios and the frothing in the gas/liquid separator which appears to introduce a time dependance to the absorbance response, necessitating frequent recalibration. Some work with anti-foaming agents may help resolve the latter problem, the former might be solved by spiking samples containing low levels of As(III) with more As(III) so the resulting As(V)/As(III) ratio will be less than 20:1, which was determined in this work to be the maximum level at which there was no distinguishable recovery of As(V).

Estimation of recovery was made only through validation of the calibration curve using in-house standards as the U.S. EPA does not provide arsenic (III) standards. Recoveries were generally poor, with response dropping as low as 60% within 20 minutes of calibration. It was possible to compensate slightly for this by using an approximate time weighted average to calculate concentrations from absorbances between calibration curves. These were validated by running separately prepared samples of known concentration at 5 minute intervals. Unfortunately, that showed that there was a tendancy to overcompensate in this fashion. Consequently no such manipulation of the data was practised.

The calibration curve presented in Figure 5.2 was prepared from standards analysed on September 29, 1989. It shows that the linear range continues to much higher concentrations compared to the total arsenic calibration. It is also apparent that the 95% confidence interval is much

Figure 5.2

Typical As(III) Calibration Curve
(66a, Sept. 29, 1990)



wider, generally ±6% at the narrowest width (10-12 µg/L for these data). The detection limit (3σ) is at an absorbance response of 0.017 which corresponds to 1.0 µg/L (compared to 0.25 µg/L for total arsenic).

The data presented in Table 5.5 were collected from samples analysed on October 1, 1989. The results are listed in the order in which they were presented to the AAS for analysis to illustrate the time dependence of the response. To give an idea of the effect of the time delay, consider an average delay of two minutes between completing sample runs. By the end of the run the calibration standards were triggering only 59% to 68% of the response they had caused earlier. The 5 µg/L validation standard exhibited suppressed response and the measured response from the 15 µg/L standard was less than its predicted (extrapolated) value, making it clear that all of the samples suffered from inhibited response. Thus these values for As(III) concentration should be considered to be low values. On the other hand, the standard spiked with As(V) does appear to show slightly higher response than the 5 µg/L calibration standard which was run immediately afterward. This may indicate that the presence of As(V) is causing an enhanced response. However this is impossible to quantify with the limited data available.

5.1.3 Arsenic (V) to Arsenic (III) Ratios

In Table 5.6 there is a summary of As(V) and As(III) concentrations for the few samples for which both are available, with the calculated As(V)/As(III) ratio. The 95% confidence interval is calculated by the method presented in Holman (1978).

Table 5.5

Typical Results (68a, Oct. 1, 1989)

Sample Label	Mean Absorbance	Mean Concentration (µg/L)	Dilution factor	Mean Concentration (mg/L)	Minimum Concentration * (mg/L)	Maximum Concentration * (mg/L)
0 µg/L	0.0002	0.00	1.0	0.000	0.000	0.000
5 µg/L	0.0931	5.00	20.0	0.100	0.093	0.107
7 µg/L	0.1246	7.00	14.3	0.100	0.095	0.105
10 µg/L	0.1653	10.00	10.0	0.100	0.096	0.104
12 µg/L	0.1882	12.00	8.33	0.100	0.094	0.106
°° Pre-Aeration	0.2878	--	50.0	Out	of	Range
Barrel	0.0049	0.26	10	Less than	Detection	Limit
Barren 9/29	0	0	100	Less than	Detection	Limit
°~ 15 µg/L	0.1986	13.02	6.67	0.087	0.079	0.095
Solids Ret'n Pond	0	0	100	Less than	Detection	Limit
Pond 1 9/29	0.0770	4.05	10.0	0.041	0.037	0.044
Pond 1 9/29	0.0732	3.83	10.0	0.038	0.035	0.042
° Pond 2 9/29	0.1258	7.08	1	0.007	0.007	0.007
Pond 2 10/1	0.1308	7.42	1	0.007	0.007	0.007
Pond 1 10/1	0.0795	4.19	10	0.042	0.039	0.045
Barren 10/1	0.1337	7.62	100	0.762	0.724	0.802
Tails	0.1324	7.53	100	0.753	0.716	0.791
Barren 10/1	0.0232	1.16	500	0.582	0.419	0.748
5 µg/L	0.0642	3.33	20	0.067	0.060	0.073
Pond 2 10/1	0.1137	6.28	1	0.006	0.006	0.007
Pond 2 10/1	0.1155	6.40	1	0.006	0.006	0.007
° Pond 1 9/29	0.0629	3.26	10	0.033	0.030	0.036
5 µg As(III)/L + 95 µg As(V)/L	0.0645	3.34	20 (as As(III))	0.067	0.061	0.073
°5 µg/L	0.0577	2.97	20	0.059	0.053	0.066
7 µg/L	0.0880	4.69	14.3	0.067	0.062	0.072
10 µg/L	0.1221	6.83	10	0.068	0.065	0.072
12 µg/L	0.1385	7.96	8.33	0.066	0.063	0.069

* based on 95% confidence limit

° Indicates that a blank was run

Table 5.6

Typical Results (66a, 68a &73a, Sept. 29, Oct. 1, 1989)

Sample Location and Date	Arsenic (V) Concentration (mg/L)	Arsenic (III) Concentration (mg/L)	As(V)/As(III) Ratio	Confidence interval of ratio (95%)
Pre Aeration Tank #2 9/29	4.64	0.462	10.0	±2.5
Barren 10/1	21.4	0.762	28.1	±2.1
Pond 1 9/29	2.61	0.0403	64.8	±6.1
Pond 2 9/29	0.240	0.0071	33.8	±3.0
Pond 2 10/1	0.298	0.0067	44.5	±3.9

Although the data presented here requires further validation, some preliminary analyses can be made. It is interesting to note the relative amounts of As(III) and As(V) throughout the system. In the Pre Aeration tanks nearly 10% of the arsenic in solution is present as As(III). This is presumably as a result of the dissolution of arsenic from the arsenopyrite in the form of As(III). Further through the process, i.e., in the Barren solution, there is considerably more dissolved arsenic, but nearly 97% is oxidized to As(V). By the time the arsenic reaches the tailings pond very little (less than 2%) remains as As(III). The dramatic drop in As(V)/As(III) ratio after treating the tailings water is because of the greater affinity and hence preferential removal of As(V) by iron hydroxides (Pierce and Moore, 1982). Some of the As(III) is removed, and some continues to be oxidized, resulting in the very low levels of As(III) in Pond 2 water. It would be interesting to monitor As(III) levels in Pond 2 from the end of the treatment phase in August to the time of discharge in July to try and estimate the rate of As(III) oxidation in Pond 2. There would be a number of competing factors affecting this rate including photolytic transformations (Brockbank, et al., 1988), biological transformation (Ehrlich, 1981) and chemical reactions which would be highly dependent on the redox conditions resulting from dissolved oxygen levels

relating to ice cover. In addition, total arsenic levels would be expected to alter through the year, affecting the As(V)/As(III) ratio. The major factors would likely be natural decomposition of ferro-cyanide compounds, which would release ferric ions which would then precipitate out and remove arsenic. The seepage of untreated tailings from Pond 1 through the saturated portion of J-dam (see Figure 2.2) would be the competing factor.

The extensive time requirements for the development and validation of the As(III) method has resulted in a rather limited pool of As(III) data. Thus reference cannnot be made to specific values for As(III) nor to As(V)/As(III) ratios, however, it is possible to make general comments about the relative occurence of these two valences in the process water and tailings at Lupin. The total arsenic method is well established, while the method for arsenic (III) requires further work to correct for poor recoveries and interference from high levels of As(V) when analysing for low levels of As(III) (at As(V)/As(III) greater than 20:1). Only early through the leaching process does As(III) constitute a significant portion of the total arsenic, elsewhere there is a substantially lower proportion of As(III).

In summary, total arsenic levels can be measured with an accuracy of ±10% with a precision of ±6% with the method and statistical analyses used in this work. The measured arsenic (III) concentration of any of the samples analysed can be taken to be at least 60% of the true value, judging by the loss in response of the standards, depending on when the sample was analysed with respect to the calibration standards and also depending on the amount of arsenic (V) which was recovered.

5.2 Bioassay Results

Two sets of LC_{50} determinations were made in order to try and estimate the relative lethality of As(V) and As(III) in the matrix of Lupin's Pond 2 discharge. The data collected in July and August were in good agreement for both toxicants. Figures 5.3 to 5.6 summarize the mortalities and show the dose-response curves after 24, 48, 72 and 96 hours. Note that the dose of arsenic (V) in July was too low to elicit any lethal response, except at full strength, until after 48 hours. As expected, the LC_{50} decreases with increasing contact time. This leads to the concept of the median (50%) threshold lethal concentration. Figure 5.7 attempts to illustrate this approximation. It involves fitting a hyperbolic curve, whereby the asymptote corresponds to the minimum dose which will cause death in half of the test organisms, regardless of the time of contact. This is still only acute contact time since many other factors (causes of death) can come into play over chronic contact times (e.g., cancer).

The range for the LC_{50}'s is an attempt to quantify a 95% confidence interval. It is based on a ±2 organisms death rate at the median death rate concentration. Standard Methods recommends at least a ±1 organism tolerance, based on a large number of test runs (APHA-AWWA-WPCF, 1989). As the 'blanks' (unadulterated Pond 2 water) used in this work experienced a mortality rate of up to two organisms and considering the limited quantity of data collected (only 6 or 7 data points total, per toxicant) it was felt that the ±2 organism tolerance was more appropriate.

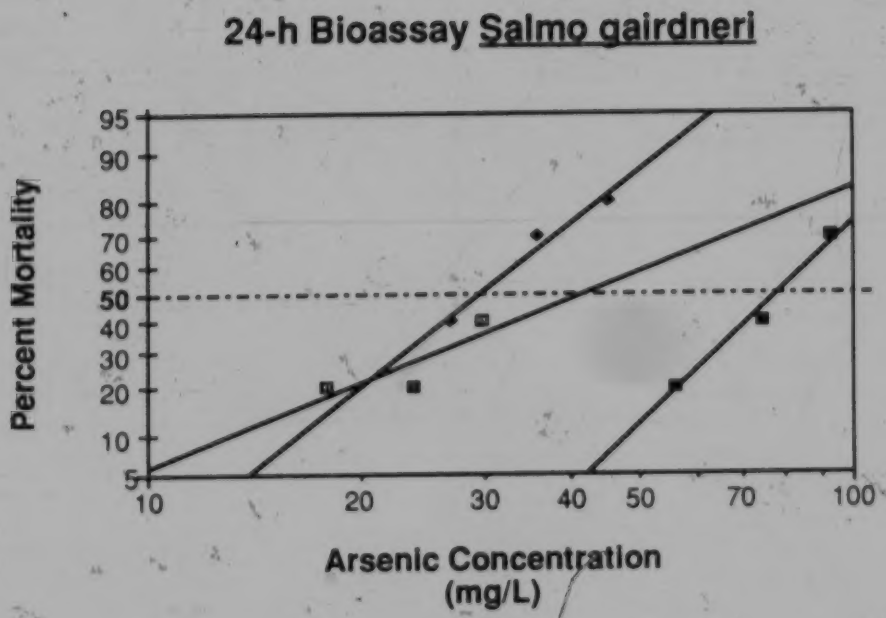
The Litchfield-Wilcoxon method is another widely used and simple nomographic method for determining the LC_{50} and its confidence limits

(APHA-AWWA-WPCF, 1989). The 'trimmed' Spearman-Karber method is statistically more rigorous than either the relatively simple probit or Litchfield-Wilcoxon analyses (Hamilton, et al., 1977). However, considering the observed mortalities in the 'blanks' it was felt that any but the simplest analysis of the data only added to the confusion.

The overall observation is that the arsenic (V) concentration required for an acute kill of half of the 1 g test specimens of *Salmo gairdneri* (46 mg/L) is about twice the required concentration of arsenic (III) (20 mg/L). This arsenic (III) LC_{50} value is in the mid-range of the literature values (14.8 to 26.6 mg/L). Unfortunately, there is little data available for arsenic (V). The ramifications of this conclusion are insignificant for Lupin as the discharge requirements are intended to protect a wide variety of biota, which may be affected over several orders of magnitude by both chronic and acute affects. As the Lupin discharge is intermittent, there may be a case for arguing the relative importance of acute versus chronic effects. However, the large As(V)/As(III) ratio in the Pond 2 discharge does not imply any heightened protection of the aquatic environment because the acute lethality of As(V) below As(III) is a mere factor of two. If As(III) was an order or two in magnitude more lethal than As(V), then the comparatively low levels of As(III) would be an advantage.

The question of chronic effects has not been addressed at all. The literature indicated an LC_0 of 0.97 mg/L over 28 days (Spehar et al., 1980 in Eisler, 1988) for arsenic (V). To ensure that there is no long term hazard, chronic studies should be started, to examine some of the common local species. The arsenic doses could even be applied annually to simulate the intermittent discharge at Lupin, although more frequent dosing would

Figure 5.3



	LC_{50}	Range	
■ As 3+ July	42	26 - 67	R^2 = 0.685
◆ As 3+ August	30	23 - 38	R^2 = 0.972
■ As 5+ August	81	71 - 86	R^2 = 0.977

Figure 5.4

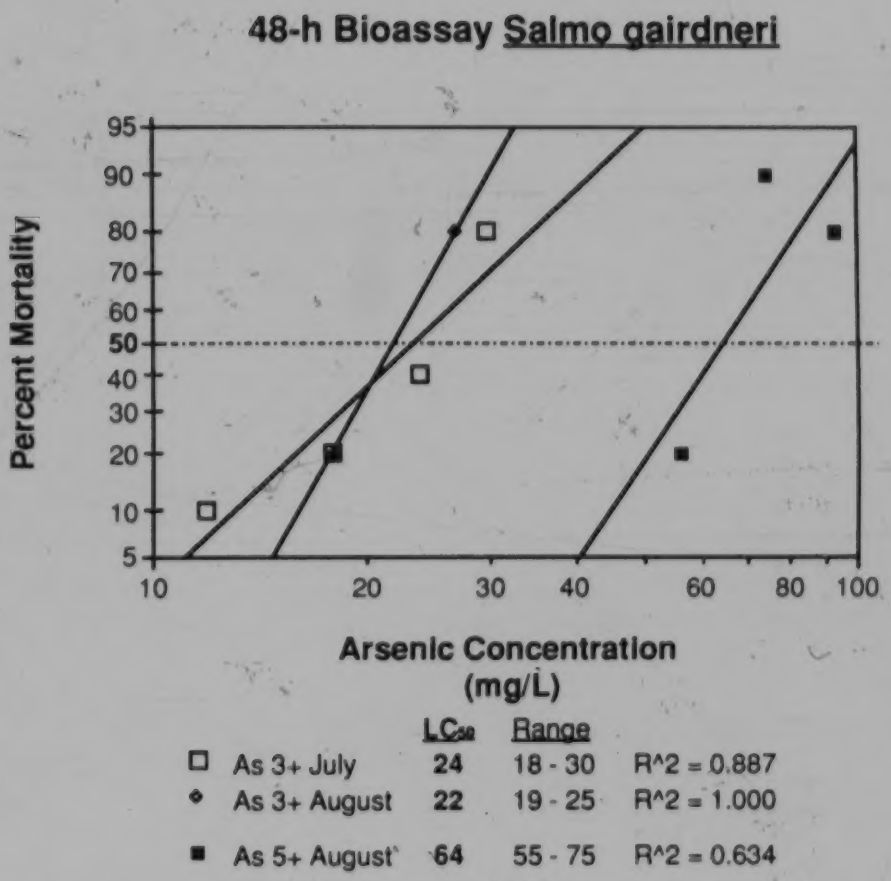
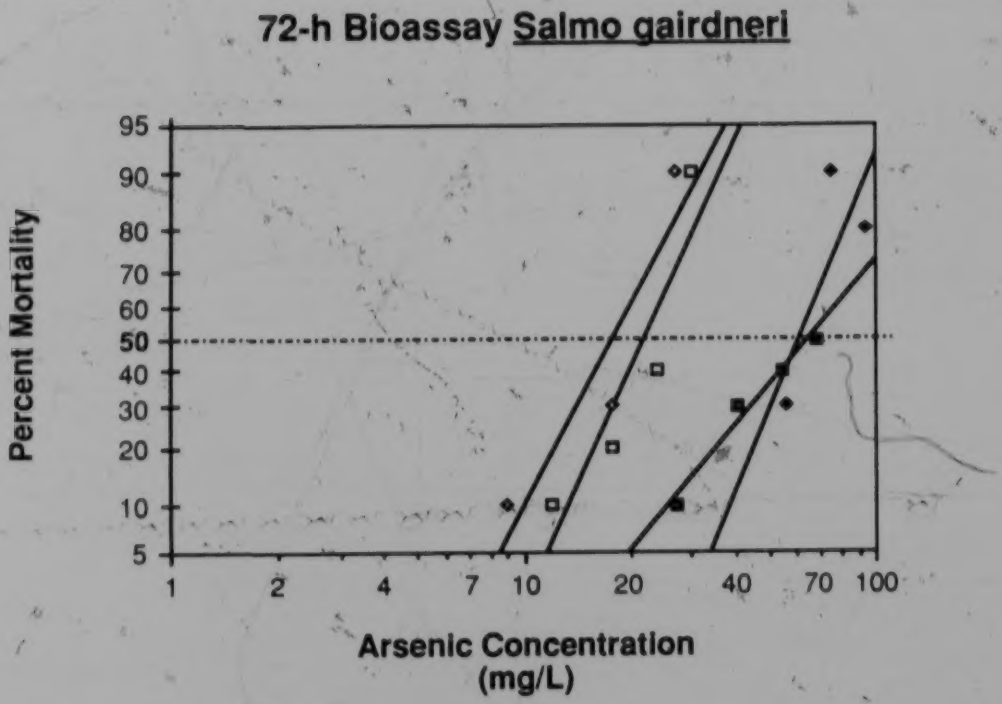

48-h Bioassay Salmo gairdneri
Percent Mortality
95
90
80
70
60
50
40
30
20
10
5
10
20
30
40
60
80
100
Arsenic Concentration
(mg/L)
LC50 Range
As 3+ July 24 18 - 30 R^2 = 0.887
As 3+ August 22 19 - 25 R^2 = 1.000
As 5+ August 64 55 - 75 R^2 = 0.634

Figure 5.5



		LC_{50}	Range	
□	As 3+ July	22	18 -27	R^2 = 0.829
◆	As 3+ August	18	14 - 22	R^2 = 0.863
■	As 5+ July	64	44 - 94	R^2 = 0.974
◆	As 5+ August	60	50 - 72	R^2 = 0.597

Figure 5.6

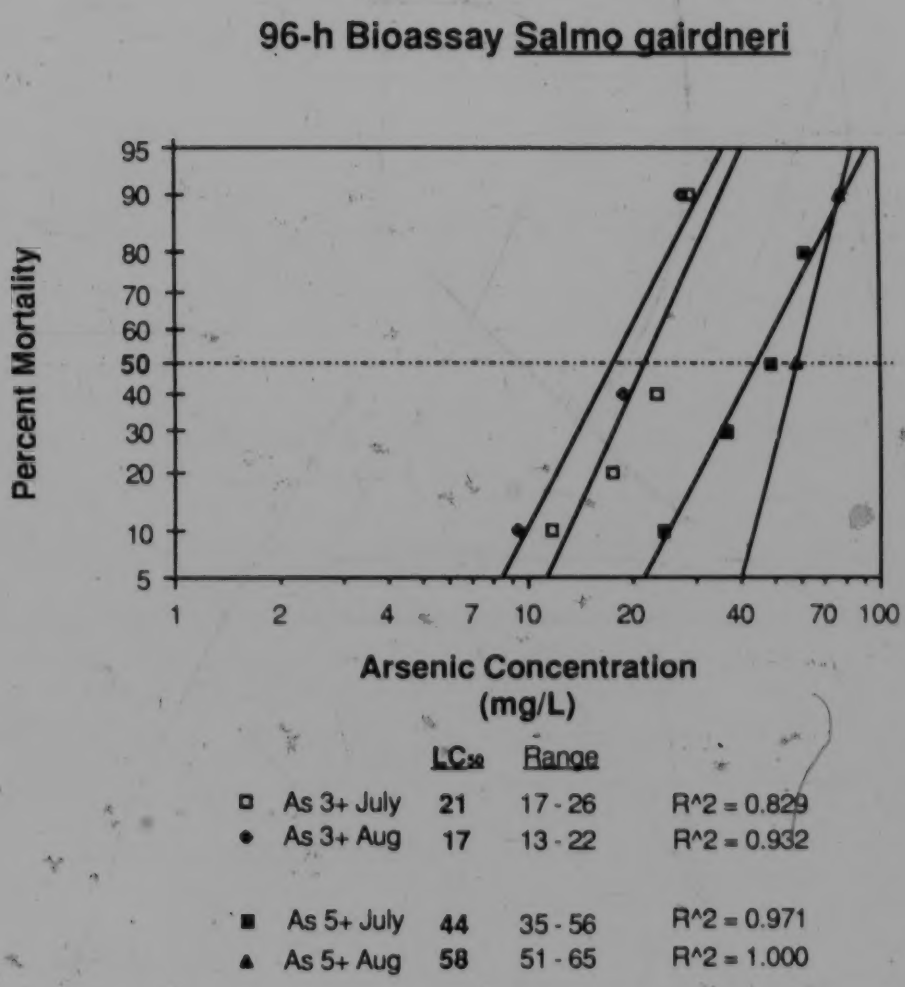
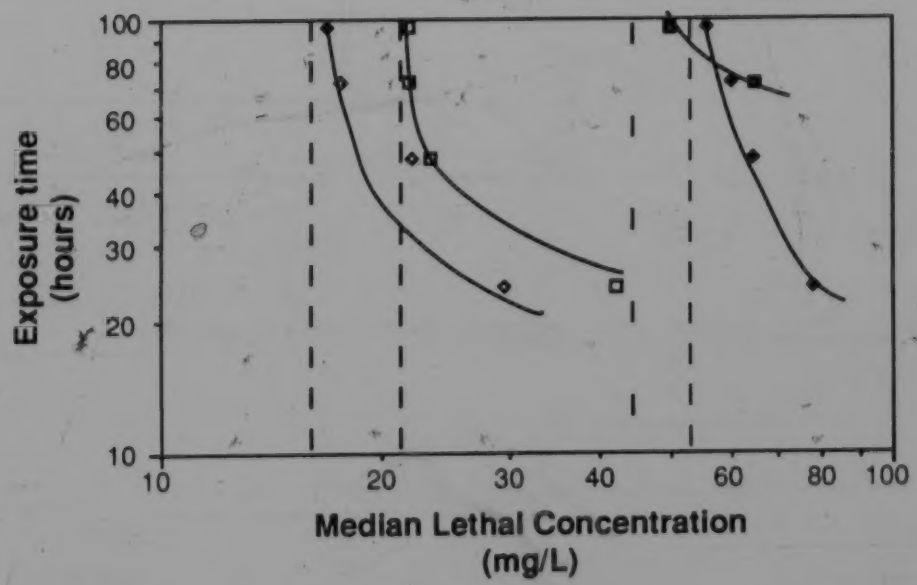

96-h Bioassay Salmo gairdneri
Percent Mortality
95
90
80
70
60
50
40
30
20
10
5
1
2
4
7
10
20
40
70
100
Arsenic Concentration (mg/L)
LC50
Range
As 3+ July 21 17 - 26 R^2 = 0.829
As 3+ Aug 17 13 - 22 R^2 = 0.932
As 5+ July 44 35 - 56 R^2 = 0.971
As 5+ Aug 58 51 - 65 R^2 = 1.000

Figure 5.7

Toxicity Curves for Salmo gairdneri



Approximate Threshold Median Lethal Concentration

□	As 3+ July	21
◇	As 3+ August	16
■	As 5+ July	46
◆	As 5+ August	53

provide a more conservative (more certain) result. In addition or as an alternative, samples of the local biota could be examined for any indication of adverse affects that may be attributable to the discharge. This should consider both aquatic and terrestrial, including both plant and animal life forms. The flora within the tailings basin has almost certainly been affected, but it may be difficult to ascertain whether this is from arsenic in the dust or the cyanide gas released from the pond water. Plants tend to reject arsenic from the soil so only plants with a large surface area are likely to be affected, through direct contact with the dust fallout.

5.3 Leach Test Results

The total recoverable arsenic and the water soluble arsenic were measured in the tails solids. The water soluble arsenic in the tails precipitate was also measured.

5.3.1 Total Recoverable Arsenic

By the use of aqua regia digestion the arsenic content of a sample of tails solids and a sample of ore were determined. Approximately 1.23% ±0.05% of a sample of ore (550 Level, West Zone) to 1.5% ±0.2% (1 s) of a sample of tailings solids (July, 23, 1989) was found to consist of arsenic. This is similar to independent analyses of tailings solids by Baum (1988) (1.05%) and Lakefield (1988) (1.2%). All analyses were made on single grab samples which may be strongly affected by the ore grade being processed at the time of sampling. There is hardly any difference in arsenic content between the ore and the tailings solids on average, because the total mass of arsenic which goes into solution in the gold extraction process is negligible. Nearly 7000

tonnes of arsenic are disposed of annually in the tailings basin in the solid phase (Table 3.1), whereas only 1 tonne per year is contained in the liquid phase.

5.3.2 Water Soluble Arsenic

The four day leach test on the tails solids and the prepared ferric hydroxide/arsenic precipitate agreed well with the qualitative results predicted from the literature. The oxidizing conditions in the shaker jars resulted in higher levels of arsenic release from the tails solids than from the precipitate. None of the samples tested showed a dissolved arsenic concentration above the 5 mg/L limit allowed by the US EPA for their extraction test. On average 0.022 ±0.007 mg As/g of tails solids and 0.009 ±0.003 mg As/g of precipitate were leached (expressed with 95% confidence interval based on triplicate leaches). The pH of the tails solids extract was quite high compared to the precipitate extract (pH 8.5 vs pH 5.3) presumably as a result of the lime residual in the tailings. This presents an important point in that the leachate from the tails solids must be kept away from the precipitate in the tailings pond, as the arsenic in the precipitate tends to desorb at pH >8 (Krause and Ettel, 1987).

5.4 Current Treatment Practices

The results of the jar tests indicate that the levels of arsenic remaining in solution are strongly dependent on dose, particularily at low iron to arsenic (Fe/As) ratios (i.e., 4:1 Fe/As). In addition an extended slow mix time was shown to have an effect similar to doubling the iron dose. Depending on the economics of the process it may be worthwhile installing a floating flocculator in the vicinity of the syphon outfall to enhance flocculation and hence

arsenic removal. Tables 5.7 and 5.8 summarize the operating conditions and the resulting arsenic concentrations for the first experimental set, while Tables 5.9 and 5.10 summarize the second experimental set.

Table 5.7

Control Parameter	+1	-1	Centrepoint
Dose	12:1	4:1	8:1
Rapid Mix (100 rpm)	200 seconds	80 seconds	140 seconds
Floc mix (80 rpm)	20 sec	20 sec	20 sec
" " (50 rpm)	15 minutes	3 minutes	9 minutes
" " (20 rpm)	15 min	15 min	15 min

Table 5.8

Dose (Fe/As mole ratio)	Rapid Mix (@ 100 rpm) (seconds)	Flocculation Mix (@ 50 rpm) (minutes)	Residual Arsenic (with 20 rpm slow mix) (mg/L)
12:1	200	15	0.20
12:1	200	3	0.20
12:1	80	15	0.20
12:1	80	3	0.24
8:1	140	9	0.40
4:1	200	15	1.00
4:1	200	3	1.36
4:1	80	15	1.06
4:1	80	3	1.79

Table 5.9

Control Parameter	+1	-1	Centrepoint
Dose	24:1	12:1	16:1
Rapid Mix (100 rpm)	80 seconds	80 seconds	80 seconds
Floc mix (80 rpm)	20 sec	20 sec	20 sec
" " (50 rpm)	9 minutes	1 minutes	5 minutes
" " (20 rpm)	0 min	0 min	0 min

Table 5.10

Dose (Fe/As mole ratio)	Flocculation Mix (@ 50 rpm) (minutes)	Residual Arsenic (without 20 rpm slow mix) (mg/L)
24:1	9	0.25
24:1	1	0.24
16:1	5	0.33
8:1	9	0.94
8:1	1	1.80

6.0 CONCLUSIONS

6.1 Arsenic Speciation

Use of the continuous hydride generation method for arsenic measurement at Lupin has shown that the concentration of arsenic in the tailings system can be determined with an accuracy of within 10% and a precision of ±6%, when operating in the optimum concentration range. This range begins at a level of at least 10 times the detection limit (usually 2-3 µg/L) to a concentration at which the calibration curve becomes excessively non-linear. This was found to be at around 16 µg/L.

Extensive method development has resulted in a method for arsenic (III) measurement that, while not without flaws, can provide an estimate of levels present. The method is an adaptation of the continuous hydride generation method used for total arsenic determination. By carefully controlling the pH during the hydride production it is possible to produce arsine (arsenic hydride) from only the arsenic (III) present in the sample.

Some of the problems encountered included a loss in signal strength (response) over time and some undesirable recovery of arsenic (V). The slight (<3%) recovery of As(V) became a significant problem at As(V)/As(III) ratios greater than 20:1. It may be rectifiable by spiking the sample with a known amount of As(III) to reduce the imbalance thus allowing the As(III) to represent a more significant portion of the total arsenic.

The loss in response over time is believed to have been caused by the entrainment of the acetate buffer into the arsine transfer tube resulting in decreased gas throughput. This was evidenced by the frequent bursting of the

connectors in the Vapour Generation Accessory. It may be possible to mitigate this problem by the addition of an anti-foaming agent.

The results from a preliminary survey of As(III) levels and As(V)/As(III) ratios show that there is very little As(III) present in solution at Lupin. The Pre Aeration tanks contained the highest percentage of As(III) (As(V)/As(III) = 10) while Pond 1 contained the lowest (As(V)/As(III) > 60). By way of comparison, the arsenic in sea water is usually 10 - 20% As(III). The decrease in the arsenic ratio in Pond 2 (As(V)/As(III) = 40) is presumably the result of the preferential adsorption of As(V) to amorphous ferric hydroxide over As(III).

6.2 Toxicity Testing

The two sets of 96-h bioassays performed on rainbow trout *Salmo gairdineri* (now *Oncorhynchus mykiss*) fingerlings showed that the LC_{50} for As(III) and As(V) differed by a factor of only two, at 23 and 46 mg/L respectively. Taking into consideration the very low levels of As(III) in the tailings ponds, it becomes clear that it is only the As(V) component that needs to be seriously considered. The current discharge limit of 0.5 mg/L is one percent of the LC_{50} for arsenic (V). This value is consistent with traditional U.S. EPA methodologies for establishing discharge limits, in the face of insufficient data, which will cause little or no significant impact on the receiving environment. To ascertain the efficacy of this discharge limit, studies should be made to verify the absence of observable impact in and around the tailings ponds and the discharge watercourses. Chronic toxicity studies should be made in the laboratory to evaluate the maximum No

Observable Effect Level. After that, evaluation of the validity of the current discharge requirement could be made.

6.3 Current Treatment

The present arsenic treatment program at Lupin is adequate for lowering the As levels to below the discharge limit. However the current procedure does not leave any allowance for upsets (e.g., introduction of untreated Pond 1 water or fresh tailings into Pond 2). If the present ferric sulphate treatment were to reduce the treated effluent concentration to a substantially lower level (e.g. the 0.2 mg/L levels achievable in the laboratory) this would provide a dilution cushion in Pond 2.

This could be done by three routes. A floating flocculator could be installed in the lagoon in the vicinity of the outfall from the syphons from Pond 1. Jar tests showed that increased slow mixing of the treated water provided reduced levels of arsenic corresponding to doubling the dosage of iron. The utility of this method would depend on the economics of the operating cost of the extra Ferri-floc versus the capital and operating costs of the flocculator. The second option is to lower the pH of Pond 1 to both decrease the cyanide levels and improve the affinity of the arsenic for the ferric hydroxide precipitate. However, because the discharge limit for Pond 2 is pH > 6, careful control of the pH would be crucial. The third possibility lies in the addition of a polymer to enhance the flocculation and settling of the hydroxide precipitate. Prior to trying any of these options, separately or in combination with each other, especially any which affect the pH (e.g. adding more Ferri-floc or other pH adjusting chemicals) it will be necessary to

evaluate, in the laboratory, the effects of those pH changes on the removal efficiencies of the arsenic by the iron.

6.4 Sediment Stability

The 4 day leach tests showed that the precipitate is much more stable under oxidizing conditions than the tails solids. It also showed that the tails solids contained residual lime which raised the pH of the leachate to pH 8.3. At this pH it could also cause the desorption of the arsenic from the precipitate as discussed in Section 7.2.1.

7.0 RECOMMENDATIONS

7.1 Further Study

7.1.1 Arsenic Speciation

The main areas for total arsenic analysis that remain to be examined are the areas of organic arsenic compounds and the presence of interferences. For the organic arsenic, some comparative analyses to evaluate the recovery of organic arsenic by the method at hand as compared to using a prior digestion step would be useful. This will provide background data for a time when organic constituents may become a significant portion of the total contamination or for evaluating arsenic in the sewage lagoons and sewage drainage.

For arsenic (III), the method should be refined by experimenting with anti-foaming agents and other mechanisms for mitigating the time dependence of the absorbance response. Work should also be done with spiking samples with As(III) to minimize the effects of the undesired recovery of As(V). Either with or without additional method development, further sampling and analysis of the process streams and tailings ponds should be made to verify the As(III) levels and to try and discover any seasonal variations in arsenic speciation. Microbiological evaluation of the pond water would help to clarify the cause of any changes in the relative abundance of the various arsenic species.

Once all of the process streams and tailings ponds are well characterized it would be extremely useful to perform mass balances on the various unit operations throughout the system to evaluate the sources and

sinks of the arsenic in its various forms. This would then provide insight to areas in the process where arsenic dissolution could be minimized.

7.1.2 Toxicity Testing

A careful study of the flora and fauna in and around the tailings ponds and the discharge watercourse should be made to evaluate the degree of impact the contaminants in the tailings have had. A thorough attempt should be made to evaluate the causative chemicals of any observable impacts. It is clear that the flora in the immediate vicinity of the tailings ponds has been impacted, although most likely by HCN gas. This will provide a base for comparing with other less affected organisms in the area.

In addition, chronic toxicity testing should be started to quantify a No Observable Effect threshold for some of the important and/or sensitive species in the area. These studies should examine both As(III) and As(V). There may be merit in attempting to evaluate any synergistic or antagonistic effects which exist with the other contaminants in the discharge, such as copper, zinc and cyanide.

7.1.3 Sediment Stability

The precipitate formed at the arsenic treatment stage is uncommon. This is because it is formed from low concentrations of dissolved iron and arsenic yet has a relatively high arsenic content, compared to natural sediment. The Fe/As ratio is only an estimate based on dosages and is not well studied. The literature reviewed has not examined this particular type of material, although extrapolations to apply the literature can be made.

The subject of the specific kinetics of microbially mediated leaching on Lupin tails has not been fully addressed. The studies of leaching kinetics reported in the literature were all performed at 20-38°C, whereas the temperature of the tailings pond does not usually get above 12°C. Some *in situ* leach tests may prove highly informative. Since the tailings ponds are ice free and warm for only a couple of months, a 60 day leach study would indicate how much arsenic would likely be released over a summer. A reasonable approximation could be made of solid to liquid ratios by using an amount of water equivalent to the average rainfall during the summer months. Depending on the percolation rate and the depth of material to be leached, the precipitation period could be selected accordingly (i.e. the deeper the bed the longer the precipitation period). The information gained from this study may help to estimate the amount of infiltration from Pond 1 by performing a mass balance on the arsenic.

Prior to performing leach tests, some microbiological evaluation should be made to attempt to classify microbial genera and populations of relevant species. If the populations are very low there may be a substantial lag time before leaching becomes apparent (e.g., several years) because of competition for substrate or nutrients. This would justify deliberately inoculating the material to be leached with some appropriate bacteria, since, over time, significant releases will occur, even at low temperatures.

A study of strictly chemical leaching could be done simultaneously, using sterilized material. This should also be done at Lupin ambient temperatures for the duration of the ice free period. Weekly sampling of the liquid phase would help in determining chemical reaction kinetics.

Short term leach tests could be run, on both the tails solids and the treatment precipitate, separately and, especially, in combination, during the time the arsenic treatment facility is in operation. Fresh precipitate could be collected the first day of operation and then leached over the remainder of the available time. For this study of chemical leaching a standard (20:1) liquid to solid ratio could be selected.

7.2 Preventative Measures

7.2.1 Sediment Stability

From the literature reviewed it is evident that there are some basic precautions that can be taken to prevent wholesale leaching of arsenic from the tailings.

First and foremost is the need to keep the tails solids and the arsenic treatment precipitate separate. The reactions between these two minerals result in the reduction of the ferric ions in the precipitate, releasing arsenic due to the higher solubility of ferrous hydroxide, and the oxidation of the arsenopyrite in the tails solids, again releasing formerly insoluble arsenic. In the absence of any microbial action, this reaction would eventually slow once most of the precipitate had dissolved. By this point some 20 metric tonnes (at an accumulation rate in Pond 2 of 1 tonne per year over the 20 year life of the mine) would have been released to the environment. This is rather significant compared to the roughly 250 kg discharged annually from Pond 2. It is also essential to keep the runoff from the tails solids away from the treatment precipitate, since the lime in the tails solids will raise the pH of the

runoff to high levels which will result in the desorption of the arsenic from the iron precipitate.

Secondly, microbial action on the tails solids needs to be minimized. This will help prevent 'acid mine drainage' contaminated with arsenic. By maximizing the depth of the surface cover, and crowning the cover to improve surface drainage, the underlying solids should remain frozen year round which will contribute greatly to mitigating this potential hazard. However it is important to remember that the types of microorganisms expected to be important are very hardy and can easily remain dormant in the frozen solids until conditions conducive to growth and reproduction come about (Emde, 1990). Keeping the tails solids free from air will not make a difference as these organisms are microaerophiles and require very little oxygen to thrive.

Preventing seepage of surface water through the the tails solids is only part of the process for minimizing microbial growth. The chemical oxidation that will occur is significantly less than the bacterial oxidation.

The arsenic treatment precipitate must also be stored to minimize microbial action. Mok and Wai (1989) experienced a release of 7.6% of the arsenic present in just 10 days. So once again percolation of water through the precipitate should be prevented. However, with this material it is crucial to avoid anaerobic conditions. The data of Brannon and Patrick (1987) indicated the release of 50% to 70% of the adsorbed arsenic at E_h= -150 mV.

When the tailings pond is taken out of commission it should be graded to provide a crowned surface. Crowning the tails will ensure proper drainage and minimize the amount of water percolating through the active layer in

the tails solids. The surface should be carefully covered to prevent wind erosion of the tails solids, because the fine particles which contain most (70%) of the arsenic are readily dispersed by the wind. The crown of the pond should not be too steep otherwise the runoff will erode the cover material, again risking exposure of the tails solids to the wind.

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